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EFFECT OF GLAZE FILM ON PROPERTIES OF A VITREOUS CHINA BODY*

By W. C. Bell and J. H. Koenig†

Abstract

Individual thermal-expansion measurements in conjunction with the tuning fork and ring glaze-fit tests have been used to establish the relation between glaze stress and its effect on the physical properties of a glazed vitreous body.

I. Introduction

A comprehensive knowledge of glaze fit is of economic importance to the ceramic industry, particularly because the stress relationship that exists between a ceramic glaze and body affects the physical properties of the glazed body.

The thermal expansion and elasticity of the body and glaze govern the amount and nature of the stress setup between the two phases on firing. If, for example, the glaze has a greater contraction on cooling than the body, the glaze will be placed in a state of tension; if the body has the greater contraction, the glaze will be placed in a state of compression; and in case either the body or the glaze is placed under stress that reaches a critical value, failure will occur at that point.

Considerable progress has been made recently in the study of this problem, and tests for measuring glaze stress have been developed.[1] These test methods may be employed to correlate the effect of the glaze stress on the physical properties of glazed bodies.

The effect of the glaze application and its control has also been the subject of several investigations.[2]

The distribution of stress in loaded flexural and tensile test specimens is shown on Fig. 1. The stress system, which becomes visible in the transparent models used in the photoelastic polariscope, is directly applicable to ceramic materials. In the tensile strength specimen, the stress is not distributed uniformly across the failure section but tends to be concentrated at the sides because of the finite radius of curvature of the specimen. The flexural test piece initially fails in tension, and the greatest stress concentration is at the underneath surface. The greatest stress concentration in both cases is thus in or at the glaze surface.

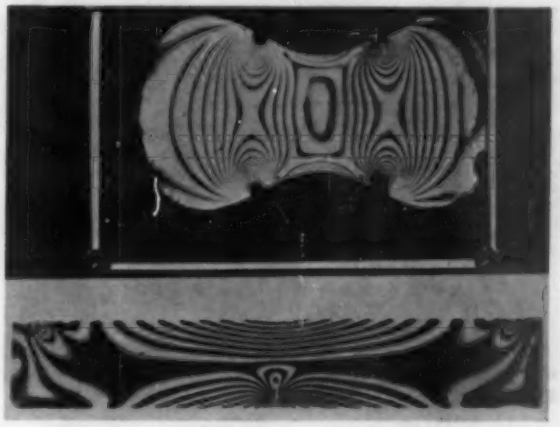

Fig. 1.—Distribution of stress in loaded flexural and tensile strength stress specimens.

Tests were conducted on the effect of the glaze condition for commercial semivitreous bodies and glazes.[3 (f)] These test specimens were bisque- and glost-fired at the respective plants. Their flexural strength values on the glazed and unglazed specimens are given in Fig. 2. The glaze application increased the strength in the greater number of cases, and no great decreases

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† Hall China Company, East Liverpool, Ohio.

[1] (*a*) W. C. Bell, "Evaluation of Glaze-Fit Test Methods," *Jour. Amer. Ceram. Soc.*, **23** [6] 163–66 (1940).

(*b*) W. Steger, "Strain in Glazed Ware and Its Detection," *Ber. deut. keram. Ges.*, **9** [4] 203–15 (1928); *Ceram. Abs.*, **7** [9] 625 (1928).

(*c*) W. Steger, "Measuring Tension in Fired Ceramic Mixes," *Ber. deut. keram. Ges.*, **11** [3] 124–52 (1930); *Ceram. Abs.*, **10** [3] 206 (1931).

(*d*) W. Steger, "Measurement of Stress by Bending of Laminated Ceramic Bodies," *Keram. Rundschau*, **40** [3] 29–33 (1932); *Ceram. Abs.*, **12** [2] 71 (1933); "Measurement of Stress in Ceramic Bodies," *Keram. Rundschau*, **45** [41] 467–72 (1937); *Ceram. Abs.*, **17** [8] 284 (1938).

(*e*) H. G. Schurecht and G. R. Pole, "Method of Measuring Strains Between Glazes and Ceramic Bodies," *Jour. Amer. Ceram. Soc.*, **13** [6] 369–75 (1930).

(*f*) H. E. Davis and R. L. Lueders, "Simplification of Ring Method for Determining Glaze Stresses," *ibid.*, **15** [1] 34–36 (1932).

(*g*) Donald Hagar, "Effect of Tremolitic Talc in Whiteware Bodies," *ibid.*, **19** [1] 14–23 (1936).

(*h*) A. M. Blakely, "Life History of a Glaze: II, Measurement of Stress in a Cooling Glaze," *ibid.*, **21** [7] 243–51 (1938).

[2] (*a*) F. H. Riddle and J. S. Laird, "Control of Glaze Fit by Means of Tensile Test Specimens," *ibid.*, **5** [8] 500–503 (1922).

(*b*) E. Gerold, "Influence of Glaze on Physical Properties of Porcelain," *Keram. Rundschau*, **33** [12] 188–90 (1925); *Ceram. Abs.*, **4** [6] 169 (1925).

(*c*) H. Handrek, "Importance of Glazes for Safe Porcelain Insulators," *Hermsdorf-Schomburg Mitt.*, 29/30, 879–93 (1926); *Herscho-Mitteilungen* 29/30, 25–29 (1927); *Keramos*, **6** [5] 184 (1927); *Ceram. Abs.*, **6** [9] 392 (1927).

(*d*) D. H. Rowland, "Influence of Glaze on Insulator Strength and Recent Improvement in High-Voltage Insulator Design," *Gen. Elec. Rev.*, **32**, 136–38 (1929); **33**, 384–87 (1930); *Ceram. Abs.*, **8** [9] 666 (1929).

(*e*) L. E. Thiess, "Influence of Glaze Composition on Mechanical Strength of Electrical Porcelain," *Jour. Amer. Ceram. Soc.*, **19** [3] 70–73 (1936).

(*f*) D. H. Rowland, "How Surface Characteristics Affect Strength of Ceramic Materials," *Ceram. Ind.*, **28** [3] 212–18 (1937); *Ceram. Abs.*, **18** [10] 273 (1939).

(*g*) J. H. Koenig, "Physical Properties of Commercial Dinnerware," *Ohio State Univ. Eng. Expt. Sta. Bull.*, No. 101, 67 pp. (May, 1939); *Ceram. Abs.*, **18** [10] 274 (1939).

(*h*) C. Bettany and H. W. Webb, "Physical Effects of Glazes: I, Effect of Glaze on Mechanical Strength of Electrical Porcelain," *Trans. Brit. Ceram. Soc.*, **39** [10] 312–35 (1940); *Ceram. Abs.*, **20** [3] 72 (1941).

were noted. These samples, however, were commercial bodies and glazes and no cases of extremely poor fits were encountered. The percentage increase or decrease in tensile and flexural strength and the crazing factor are shown in Fig. 3. The resistance to crazing was also increased when the mechanical strength was increased by the glaze application; the correlation, however, was good.

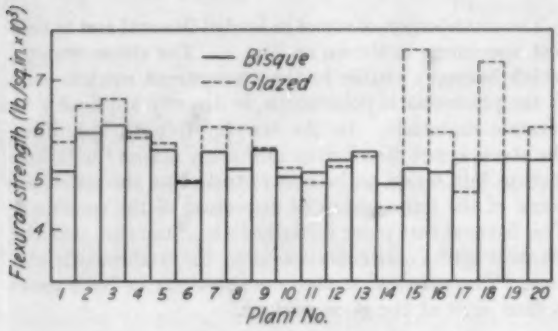

FIG. 2.—Flexural strength values on glazed and bisque semivitreous body specimens.

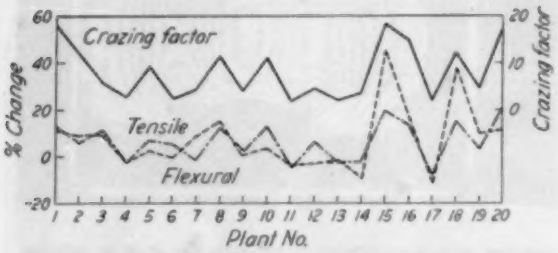

FIG. 3.—Correlation of crazing factor with percentage of change in tensile or flexural strength of bisque after glazing.

The modulus of elasticity, in general, was increased by the application of the glaze. In tests on a large number of commercial bodies and glazes, glazing generally stiffened the bisque specimen, and in eight out of nine vitreous china bodies tested, the glaze application increased the modulus of elasticity of the bisque.[2(g)] Concurrently, an increase in strength was noted except in one case, and this particular glaze was the lowest in compression. By glazing the bars, first one side, then two sides on the top and bottom, and finally all over, the flexural strength and modulus of elasticity were progressively increased for a glaze in fair compression. Repeating this experiment on the same body with a glaze in low compression did not show any orderly improvement either in strength or in elastic modulus.

II. Purpose of Present Work

Previous work failed to correlate fully the thermal expansion and glaze stress with the resultant physical properties of glazed ware. In most of the previous work, glaze thermal-expansion determinations were carried only to 400° or 500°C.

The thermal-expansion procedure usually employed was not suitable for complete accuracy, and satisfactory direct stress determination methods were seldom used. (A number of investigators have been unable to establish a very definite relationship between thermal-expansion values and physical properties.) The maximum glaze compression desirable for the best glaze fit, moreover, was another point for study.

The aim of this work has been to employ, comprehensively, the various glaze-fit methods as tools to study the effects of glazes on glazed ware and to establish a procedure in developing glazes of good physical properties.

III. Procedure

The three glaze-fit test methods employed were the individual thermal-expansion determinations, the ring test, and the tuning-fork test.

All thermal-expansion determinations were made by the interferometric method.[3] The test procedure as developed by Saunders[3(d)] was followed. V-shaped specimens were cut from the bars for bisque expansion determinations. Glaze chips, approximately 0.04 in. thick, were taken from glazed bars for expansion measurements. Special test specimens were made for this test on which the glazes were applied somewhat thicker than for the other specimens of normal glaze application (the latter glaze was approximately 0.015 to 0.020 in. thick). The body was ground from the chip, leaving as much as possible of the glaze-body interface. The specimens were given a preheat treatment to 300°C. in the interferometer. A heating rate of 3° to 3.5°C. per minute was used in the thermal-expansion measurements. A 2-gm. platinum weight was employed for the specimen loading.

For the ring test, cast rings were used which were approximately $2^3/_4$ in. in outside diameter and $^1/_4$ in. in wall thickness.[1(a, e, f)] Microscopic cross lines on brass tabs were used as reference points, and a micrometer microscope was used for the readings. This measuring instrument was accurate to 0.002 mm., and readings could be duplicated easily to 0.01 mm.

Cast tuning forks were used with dimensions as recommended by Blakely.[1(b)] The test procedure closely followed that of Blakely, although a horizontal type of test furnace was used in order to attain an even distribution of the heat. A heating rate of $2^1/_2$° to 3°C. per minute was used.

[3] (*a*) G. E. Merritt and C. G. Peters, "Interferometer Measurements of the Thermal Dilatation of Glazed Ware," *Jour. Amer. Ceram. Soc.*, **9** [6] 327–42 (1926).

(*b*) G. E. Merritt, "Interference Method of Measuring Thermal Expansion," *Bur. Stand. Jour. Research*, **10** [1] 59–76 (1933); R.P. 515; *Ceram. Abs.*, **12** [3] 129 (1933).

(*c*) G. E. Merritt, "Application of Interferometer to Measurements of Thermal Dilatation of Ceramic Materials," *Bur. Stand. Sci. Paper*, No. 485, 17 pp. (March, 1924); *Ceram. Abs.*, **3** [6] 200 (1924).

(*d*) J. B. Saunders, "Improved Interferometric Procedure as Applied to Expansion Measurements," *Jour. Research Nat. Bur. Standards*, **23** [1] 179–95 (1939); R.P. 1227; *Ceram. Abs.*, **18** [11] 306 (1939).

(*e*) C. J. Kinzie and C. H. Commons, Jr., "Discussion Relating to Thermal-Expansion Methods from Theoretical and Practical Standpoints," *Jour. Amer. Ceram. Soc.*, **18** [10] 306–308 (1935).

Details of the furnace are shown in Fig. 4. A vertical type of test furnace was built for this test work. It had the serious disadvantage, however, of a definite stack action, that is, as the temperature was increased above 300°C., the top section of the tube had a tendency to become hotter than the lower section. This trend became more marked as the temperature increased. To obtain an even heat distribution over the length of a vertical furnace, it would be necessary to wind the furnace in several sections and to use a variable resistance that could be adjusted for the different sections.

The horizontal tube construction eliminated the problem of stack action and simplified the furnace winding problem. An almost uniform winding of the core was used, except for an extra turn of wire at the observation window and the omission of one turn of wire between the observation window and the open end of the furnace. Fourteen feet of No. 16 gauge Chromel A resistance wire, which served as the heating element, was wound with a spacing of five turns per inch of core. The variation in temperature at any point in the test area of the furnace was never more than 3.5°C. over the entire cycle.

The observation window (Fig. 4) was made as small as possible to minimize the heat loss at that point, and a small spotlight was used to observe the specimen. Two 1/8-in. Pyrex-brand glass windows, placed in the furnace at such an angle as to decrease the light reflectance, served also to decrease the heat loss.

The test specimen was fitted into a porcelain holder, which extended through the open end of the furnace and was clamped to an adjustable rod that could be moved in any direction. The specimen was always adjusted to the horizontal with reference to the observing telescope. The ends of the test pieces were ground to close dimensions to insure a good fit in the porcelain holder, and small dots of chrome oxide were used as reference points. The telescope was accurate to 0.01 mm., and readings could be checked to ±0.01 mm. Satisfactory results were obtained with this arrangement.

Tests for flexural strength and thermal endurance were chosen as representative for the study of physical properties. Extruded bars, approximately 7/8 in. square (with the corners slightly rounded), were used for the flexural strength measurement. The glazes were applied by dipping carefully to obtain a normal and uniform application. One end of the specimen was left unglazed for convenience in firing, and all bars were fired in a vertical position. The data obtained represent the average of 15 determinations. The variation of the strength data was seen to be greater when the particular glaze was in tension or in low compression than when it was in high compression.

Round extruded bars, 3/4 in. in diameter, were used for the thermal-shock test. These bars were glazed and fired in the same manner as the flexural strength pieces. The bars were transferred from the oven to the water by a light metal frame which held 16 specimens evenly spaced in a circular fashion. Only about three fourths of the glazed bar was placed in the water;

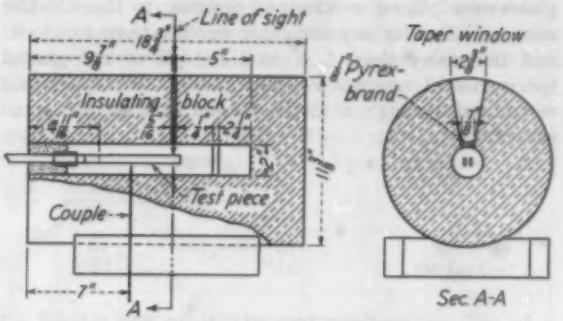

FIG. 4.—Tuning-fork test furnace.

the unglazed portion remained out of the water and thus was not subject to severe shock. The following scheme was used to record the data, which represent the average of tests on ten specimens:

No. of specimens	Passed / Failed	No. of cycles

For example, 3(f)6 at a definite temperature means that three bars failed on the sixth cycle at that temperature; 2(p)3 means that two specimens passed the third cycle at a definite temperature. The following tabular setup was used to assign a numerical value to the thermal-endurance data:

Temp. range (°F.)	Failure on cycle No.	Value
350–80	1	1
	2	2
	3	3*
400–80	1	8 (6 + 2)
	2	10
	3	12*
450–80	1	21 (18 + 3)
	2	24
	3	27*
500–80	1	40 (36 + 4)
	2	44
	3	48*
550–80	1	65 (60 + 5)
	2	70
	3	75

* Etc., up to 6 cycles.

All glazed specimens were thus subjected to six cycles at one temperature before they were tested at a higher temperature except for glaze A of set No. 1, which was initially crazed at the cone 11 fire; although no initial crazing occurred on this glaze at cone 13, it failed in thermal shock on the first cycle at 265°F. By using the foregoing scheme to calculate the factors, this glaze obviously would have a negative value.

The specimens were fired so as to insure as uniform a thermal treatment as possible. Two sets of glazes were fired and treated separately; bisque specimens were fired along with each set. For each glaze, there were 15 flexural-strength specimens, 10 thermal-shock specimens, 4 rings, 3 tuning forks, and the glaze-expansion specimens. The flexural test specimens were placed in a straight line across the kiln car from side to side; the thermal-shock specimens were placed in a similar manner; and the other specimens with the same

glaze were placed as close as possible to these. The cone variation for any one glaze was less than 1 o'clock, and not more than 1 o'clock for all of the glazed specimens of one set on one firing. All specimens were fired through a muffle tunnel kiln on the same schedule.

	Cone deformation firing	
	Low	High
First set	12^1	13^3
Second set	11^6	13^1

In addition to these two sets, there was a third set of thirteen glazes. The same glazing and firing procedure was used with a temperature of cone 13^1.

IV. Discussion of Results

(1) Thermal-Expansion Test

Each of the glaze-fit test methods has a particular advantage. The thermal-expansion test affords an explanation as to the independent expansion behavior of the glaze and body. It is not a precise glaze-stress test because it does not show all of the thermophysical characteristics of the glaze and body. It is difficult to comprehend the full importance of changes in viscosity, rigidity, internal friction, or in the presence of plastic flow in glazes[4] although these properties materially affect the stress that exists between the glaze and the body. Thermal expansion, however, is one of the most important factors that governs the glaze-body stress relationship.

This test requires considerable care in obtaining a precise determination. The glaze thickness used for the test was slightly greater than that used for the other tests, but it is felt that the data obtained closely approach the true expansion value of the glaze on the other specimens. Good check results were obtained by the use of the Saunders' procedure.

Figure 5 shows the thermal-expansion curves for the vitreous body and five glazes of the first set, which were fired to cone 12^1. The glaze expansion for each specimen is shown up to its softening point. For convenience, the glaze in this group with a maximum thermal expansion at 650°C. was labeled glaze A with that of the lowest, glaze E. Glaze A was initially crazed, and it is obvious from the thermal expansion that this glaze is under tension. The other glazes show varying degrees of compression.

There are several points of particular interest to be observed in Fig. 5. The rapid increase in thermal expansion for some of the glazes just before the softening point is reached is generally termed the "transformation." The amount of increase varies for the different glazes, and in one case (glaze E), it appears to be negligible or absent. This characteristic apparently depends principally on the structure of the glaze, which in turn is dependent on its composition. Part of its behavior is also affected by its maturing temperature and rate of cooling.[5] Glaze B, which is highest in feldspar, has the greatest transformation increase.

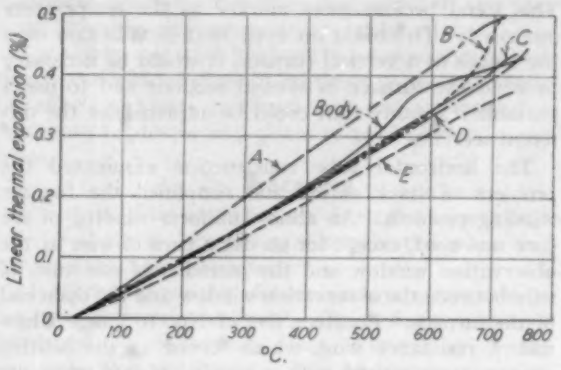

FIG. 5.—Thermal-expansion curves of a vitreous body and glazes fired to cone 12^1.

Part of the apparent stress that is set up in glaze B obviously must be dissipated or relieved in the glaze by some form of plastic flow. It is interesting to note that although glaze B has a greater total expansion than glaze A, the former glaze is in slight compression with reference to the body whereas glaze A is in tension; this shows that other glaze characteristics, in addition to thermal expansion, must also be considered.[6] It would be difficult, therefore, to determine the actual stress development in the glaze by the thermal-expansion behavior alone.

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[4] (*a*) F. B. Birch and D. Bancroft, "Rigidity and Internal Friction of a Glass in Its Softening Range," *Bull. Amer. Phys. Soc.*, **16** [1] 8 (1941).

(*b*) W. Steger, "New Investigations on Thermal Expansion and Annealing Temperature of Glazes with Special Reference to Fitting Glazes to Bodies," *Ber. deut. keram. Ges.*, **8** [1] 24–43 (1927); *Ceram. Abs.*, **6** [7] 293 (1927).

[5] (*a*) C. G. Peters and C. H. Cragoe, "Measurements of Thermal Dilatation of Glass at High Temperatures," *Bur. Stand. Sci. Paper*, No. 393, 39 pp. (1920); *Ceram. Abs.* in *Jour. Amer. Ceram. Soc.*, **3** [10] 852 (1920).

(*b*) A. Q. Tool and J. Valasek, "Concerning the Annealing and Characteristics of Glass," *Bur. Stand. Sci. Paper*, No. 358, 35 pp. (1920); *Ceram. Abs.* in *Jour. Amer. Ceram. Soc.*, **3** [5] 417 (1920).

(*c*) P. Lafon, "Anomalies in the Expansion of Glass," *Compt. Rend.*, **175**, 955–58 (1922); *Ceram. Abs.* **2** [6] 125 (1923).

(*d*) G. S. Parks, H. M. Huffmann, and F. R. Cattoir, "Studies on Glass: II, Transition Between Glassy and Liquid States in the Case of Glucose," *Jour. Phys. Chem.*, **32**, 1366 (1928).

(*e*) W. E. S. Turner and F. Winks, "Expansion of Glass: I, General Form of Expansion Curve; II, Glasses of the Series Sodium Metasilicate," *Jour. Soc. Glass Tech.*, **14** [53] 84–109; 110–26T (1930); *Ceram. Abs.*, **9** [9] 721–22 (1930).

(*f*) Gustav Keppeler, "Glazes in Ceramics," *Ber. deut. keram. Ges.*, **14** [8] 327–43 (1933); *Ceram. Abs.*, **13** [3] 66 (1934).

[6] (*a*) J. R. Clarke and W. E. S. Turner, "Influence of Lime on Value of Young's Modulus of Elasticity for Soda-Lime Glasses," *Jour. Soc. Glass Tech.*, **3**, 260–66T (1919).

(*b*) W. Steger, "Elastic Modulus of Glazes," *Keram. Rundschau*, **27**, 313–16 (1919); *Ceram. Abs.* in *Jour. Amer. Ceram. Soc.*, **3** [7] 596 (1920).

(*c*) R. Rieke and W. Steger, "Determination of Elasticity of Glazes," *Keram. Rundschau*, **27**, 193–203 (1919).

(*d*) H. T. Jessop, "Cornu's Method of Determining Elastic Constants of Glass," *Phil. Mag.*, **42**, 551–68 (1921); *Ceram. Abs.*, **1** [4] 116 (1922).

The behavior of glaze B brings out another interesting point when it is compared with glazes A and C. At 550°C., glaze B has a lower thermal expansion than glazes A or C, whereas at their softening points, glaze B has a slightly greater expansion than glaze A and a much greater expansion than glaze C. Glaze A is in tension; glaze B, in slight compression; and glaze C, in moderate compression. The influence of glaze thermal expansion in the transformation range is reduced somewhat due to the presence of plastic flow. It is obvious, however, that to comprehend fully all of the information on the glaze thermal expansion, data must be obtained up to the glaze softening point.

Figure 6 represents a similar set of specimens fired to cone 13[3]. The body has a lower thermal expansion at the higher fire, but the glazes also have a lower expansion. Although there are discernible variations, the relative thermal expansions are approximately in the same order as before.

A number of writers have pointed out the necessity of using glaze chips taken from the body for thermal-expansion measurements. Figures 5 and 6 seem to verify their conclusions because it is evident that thermal history and glaze-body reactions play an important part in glaze thermal expansion.

Table I shows a comparison of the glaze thermal expansions taken up to their softening points and the cubic-expansion values of the same glazes calculated by means of the Mayer and Havas factors.[6] These values are also compared with the various glaze-fit test values.

Plotting the calculated expansion coefficients versus the glaze-stress values does not give an entirely satisfactory correlation. Glaze E, for example, with the lowest calculated coefficient in this group of glazes, did have the greatest compression, but there are also irregularities in these data. The use of such factors in some cases is known to give, by calculation, values

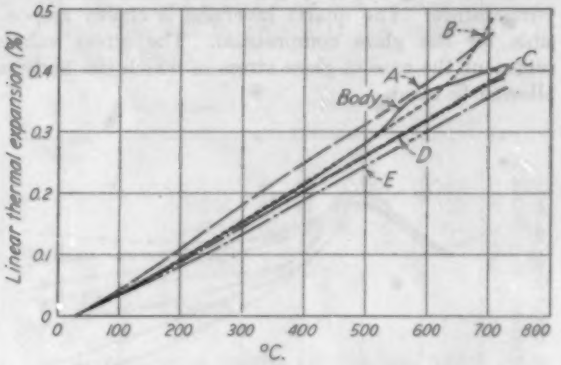

FIG. 6.—Thermal-expansion curves of body and glazes fired to cone 13[3].

which are in fair agreement with the observed values for similar composition ranges. The factors do not seem applicable to the composition range that is represented by these glazes as judged by the stress imparted to the glazes when they are fired at the same time on the same body. Such factors, however, obviously cannot cover changes in the glaze composition due to body solution and other changes resulting from thermal-treatment differences.

(2) Tuning-Fork Tests

Tuning-fork tests were run on the preceding glazes to compare the thermal-expansion values with the actual stress development in the glaze. The stress development of the glazes of the first set fired to cone 12[1] are plotted in Fig. 7, and a similar set fired to cone 13[2] is shown in Fig. 8. A comparison of thermal-expansion and stress development may be readily made from these curves.

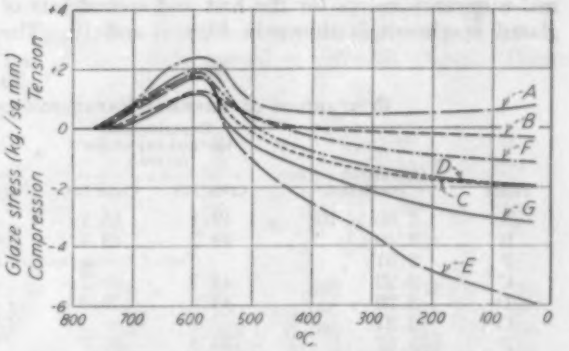

FIG. 7.—Tuning-fork stress curves at cone 12[1].

(*e*) A. Granger, "Adjustment of Body and Glaze," *Céramique*, **25** [417] 329–33 (1922).

(*f*) W. E. S. Turner and F. Winks, "Influence of Boric Oxide on Properties of Chemical and Heat-Resisting Glasses: I, Preparation and Physical Properties of the Glasses," *Jour. Soc. Glass Tech.*, **9**, 389–405T (1925).

(*g*) G. Gehlhoff and M. Thomas, "Physical Properties of Glass Related to Their Physical Composition: II, Mechanical Properties," *Z. tech. Physik.*, **7** [3] 105–26 (1926); *Ceram. Abs.*, **5** [11] 353 (1926).

(*h*) M. Samsoen, "Expansion of Glass," *Compt. Rend.*, **182**, 1384–86 (1926); *Ceram. Abs.*, **5** [10] 305 (1926).

(*i*) W. L. Shearer and W. R. Wyckoff, "Thermal Expansions of Whiteware Materials and Bodies over a Wide Temperature Range," *Ceramist*, **7** [6] 349–85 (1926); *Ceram. Abs.*, **5** [7] 223 (1926).

(*j*) S. English and W. E. S. Turner, "Relationship Between Chemical Composition and Thermal Expansion of Glasses," *Jour. Amer. Ceram. Soc.*, **10** [8] 551–60 (1927).

(*k*) Max Mayer and Béla Havas, "Coefficient of Expansion of Enamels and Their Chemical Composition," *Sprechsaal*, **42** [34] 497–99 (1909); **44** [13] 188–90; [14] 207–209; [15] 220–22 (1911).

(*l*) E. Zschimmer, "Calculation of Glass Constants on Basis of Recent Investigations," *Jour. Soc. Glass Tech.*, **12** [45] 82–118T (1928).

(*m*) L. D. Fetterolf and C. W. Parmelee, "Effects of Soda, Barium, and Zinc on Elasticity and Thermal Expansion Coefficients of Glass," *Jour. Amer. Ceram. Soc.*, **12** [3] 193–216 (1929).

(*n*) F. P. Hall, "Influence of Chemical Composition on Physical Properties of Glazes," *ibid.*, **13** [3] 182–99 (1930).

(*o*) R. Rieke, "Some Physical Properties of Whiteware Glazes," *Ber. deut. tech.-wiss. Abt. D, Ber. Keram. Gewerke*, **5** [5] 8–15 (1919).

(*p*) Hans Lehmann and M. Schulze, "Expansion Behavior of Earthenware Glazes," *Ber. deut. keram. Ges.*, **16** [1] 1–19 (1935); *Ceram. Abs.*, **14** [8] 193 (1935).

A high apparent glaze tension occurs at 600°C.; in fact, glaze A, which has less than this degree of tension at room temperature, fails by crazing. Such tension at this point, moreover, would be expected from a comparison of individual glaze and body thermal-expansion data. A definite decrease in the thermal-expansion coefficient may be observed for the body above 573°C., and in most cases an increase occurs in the glaze coefficient of expansion above this temperature. The quartz inversion is chiefly responsible for the glaze compression. The stress values represent the case of glaze stress in which the body is allowed to bend.

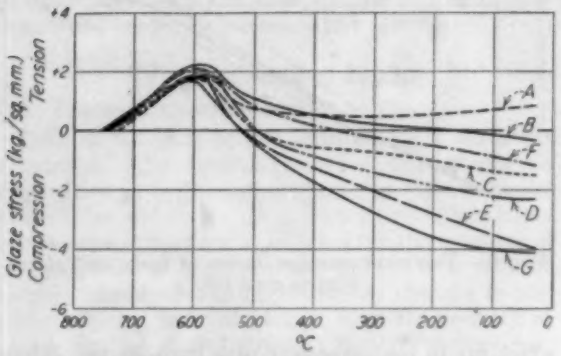

FIG. 8.—Tuning-fork stress curves at cone 13[2].

(3) Ring Tests

Ring tests were run on all of the glazes. This glaze-fit test method was considered to be the simplest method of obtaining glaze-stress values, and because only one body was used, it was also considered to be at least reasonably satisfactory to obtain comparative data.

The stress values obtained by the ring test agree well with those values obtained in the tuning-fork test. The ring values, however, are given in millimeter contraction or expansion after sawing; a positive value represents glaze tension; a negative value represents glaze compression; and the greater the negative value, the greater the glaze compression.

V. Physical Properties

A comparison of the ring, flexural strength, and thermal-endurance values for the first and second sets of glazed specimens is shown in Figs. 9 and 10. The curves to the left, in each figure, represent the data for the lower fire and those to the right represent similar data for the higher fire. The glaze stress, flexural strength, and thermal-endurance values are in agreement. The greater the glaze compression, the more these latter values are enhanced. An exact correlation, however, between all of these properties for the different glazes could hardly be expected because of the variations in glaze elasticities, discontinuities, and film thicknesses.

A comparison is shown in Fig. 11 between glaze stress, obtained by the ring method, and the flexural strength values for the third set of glazed bars (consisting of thirteen other glazes).

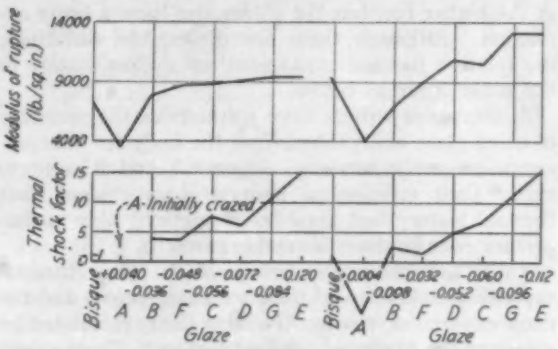

FIG. 9.—Physical properties vs. glaze compression; the ring values are +0.040 to −0.120 and +0.004 to −0.112, inclusive.

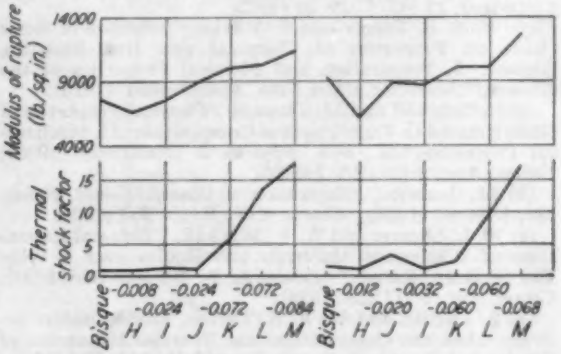

FIG. 10.—Physical properties vs. glaze stress; the ring values are −0.008 to −0.084 and −0.012 to −0.068, inclusive.

TABLE I

COMPARISON OF THERMAL-EXPANSION AND GLAZE-FIT DATA (FIRST SET OF GLAZES)

Glaze	Calculated cubic coefficient*	Experimental thermal expansion (μ/cm.)		Ring values (mm.)		Tuning fork values (kg./sq. cm.)	
		Cone 12[1]	Cone 13[2]	Cone 12[1]	Cone 13[2]	Cone 12[1]	Cone 13[2]
A	2.65×10^{-7}	49.1	45.1	(+)0.040	(+)0.004	(+)0.78	(+)0.82
B	2.49	49.7	48.3	(−)0.036	(−)0.008	(−)0.33	(−)0.41
F	2.51			(−)0.048	(−)0.032	(−)1.16	(−)1.20
C	2.22	43.7	39.2	(−)0.056	(−)0.060	(−)2.01	(−)1.53
D	2.20	44.6	39.0	(−)0.072	(−)0.052	(−)1.95	(−)2.30
G	2.21			(−)0.084	(−)0.096	(−)3.16	(−)4.17
E	1.97	36.8	36.7	(−)0.120	(−)0.112	(−)6.02	(−)4.00

* Mayer and Havas factor (see footnote 6 (*k*)).

A good correlation is found when the observed values for glaze condition are compared with changes in strength that are produced by the glaze application on the bisque. The strength is reduced for the measured low compression. This strength, however, is progressively increased with increase in the compressive stress in the glaze. Glaze No. 13 increased the strength of the bisque nearly 40%. Whatever effects are observed for the flexural strength specimens (in this instance, round bars, $^3/_4$-in. in diameter) should be accentuated for the usual ware dimensions.

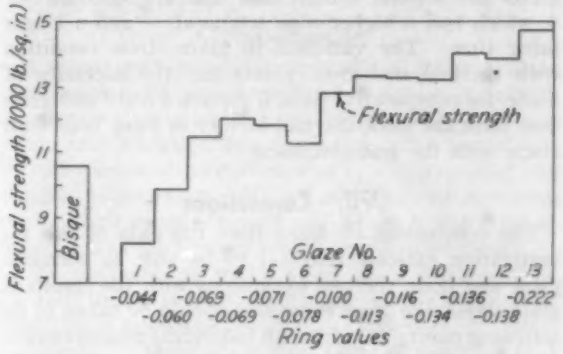

FIG. 11.—Flexural strength vs. glaze compression.

VI. Stress Condition[7] Versus Plant Variables

Good checks are attained with the ring-test measurement when the same glaze and body composition, a similar glaze thickness, and the same thermal history are involved and the necessary care is observed in the technique used. Some variation, however, may obviously exist in production when the composition and thermal treatment vary even to a limited degree.

Data were taken to show variations in a glaze-stress condition which may result from different types of plant preparation of the same glaze and of the dipping variables. Rings, which were cast from the same body slip at the same time, were dipped in a glaze; this procedure was repeated four times over a period of two months. During this time, the glazes were largely or entirely replaced frequently by new additions to the dipping tubs. Because nothing was said to the respective dippers regarding the application and agitation of the glaze or of the possible variation in the glaze composition, the factors of glaze homogeneity in the tub, film thickness, and aging changes were also involved. Five glazes were tested, and all of the rings were fired together in groups of the same glaze to cone 12^6 in 37 hours.

Compression avg. of 3 rings (mm.)

Glaze	Test interval 1	2	3	4	5
a	(−)0.180*	0.168	0.148	0.168	0.192
b	0.116	0.112	0.100	0.128	0.100
c	0.076	0.068	0.076	0.064	0.064
d	0.048	0.048	0.032	0.032	0.048
e	0.052	0.040	0.036	0.040	0.036

* All values are minus (−).

The agreement of results for the individual glaze, when the body properties and firing factors were the same, was even better than might have been anticipated. More variation would naturally occur were less attention given to the control of the glaze preparation and to routine in the dipping room.

Several tests will be described here to show variations of the glaze stress with thermal history (with other factors eliminated). In one experiment, rings (cast from the same body slip and dipped in the same glaze) were placed in thirty-six different positions on a car. Nine positions on each of four car decks were represented as follows:

NW	NC	NE
CW	CC	CE
SW	SC	SE

The cone deformation and compression values for these positions are given in Table II.

Most of the compression values and cone-deformation values were similar. The maximum variation in the compression values was from 0.064 to 0.110 mm. and in cone temperature from 12^5 to 13^4. Averages of all rings on each car deck starting with the top deck were (−)0.094, 0.092, 0.090, and 0.090 mm., respectively.

Using rings cast from the same body slip as before, sets of rings were dipped in different glazes. These

[7] (*a*) W. Steger, "Dependence of Tension in Glazed Ware on Distribution of Glaze Components in Frit and Mill Charge," *Ber. deut. keram. Ges.*, **12** [2] 43–66 (1931); *Ceram. Abs.*, **10** [6] 458 (1931).

(*b*) J. H. Benrubi, "Agreement of Mixes and Ceramic Glazes," *Verre Silicates Ind.*, **7** [6] 61–65, 73–77; [8] 90–93 (1936); *Ceram. Abs.*, **15** [7] 211 (1936).

(*c*) A. L. Johnson, "Stresses in Porcelain Glazes," *Jour. Amer. Ceram. Soc.*, **22** [11] 363–66 (1939).

TABLE II

	NW	NC	NE	CW	CC	CE	SW	SC	SE
Top deck (cone)	13^2	13^3	13^3	13^3	13^1	13^2	13^3	13^3	13^2
2nd top deck	13^4	13^3	13^3	13^3	13^2	13^3	13^4	13^3	13^2
3rd "	13^4	13^3	13^3	13^3	13^3	13^3	13^3	13^3	13^3
4th "	13^1	13^1	12^5	12^5	13^1	13^3	13^1	13^1	13^1
	(Avg. compression value)								
Top deck	(−)0.110*	0.086	0.104	0.094	0.094	0.090	0.082	0.104	0.082
2nd top	0.094	0.084	0.088	0.094	0.086	0.100	0.098	0.098	0.090
3rd "	0.098	0.088	0.076	0.092	0.090	0.092	0.094	0.094	0.084
4th "	0.064	0.092	0.102	0.080	0.092	0.076	0.104	0.098	0.100

* All values are minus (−).

were fired in various commercial kilns on different firing schedules and to different cone temperatures as follows:

Schedule (No.)	1	2	3	4
Total firing time (hr.)	42	42	37	57
Cone deformation	11[5]	13[3]	12[3]	12[4]
Glaze No.	Compression avg. of 3 rings (mm.)			
f	(−)0.016*	0.058	0.084	0.092
g	0.034		0.044	0.076
h	0.072	0.074	0.084	0.112
i	0.171	0.177	0.170	0.176
j	0.052	0.070	0.082	0.076
k	0.052	0.084	0.090	0.072
l	0.082	0.126	0.090	0.124
m	0.030	0.060	0.044	0.064

* All values are minus (−).

Schedules No. 1 and No. 2 had the same length of firing, but No. 2 was carried to a higher temperature. The compression was greater in all of these glazes at the higher firing, although this does not agree with the thermal expansion of the vitreous china body alone which is higher for the lower firing. The body is also more elastic at the lower fire but it has less strength. Judging only from body thermal-expansion data, a higher glaze compression would be predicted at the lower firing temperature. The lower glaze compression actually found, however, correlated with the poorer thermal endurance noted for specimens that received this lower temperature firing. For the low-temperature firing, it is reasoned, there is less lowering of the glaze thermal expansion from body solution or volatilization than for the higher firing. Among possible other factors which may enter into the explanation, the latter very likely is chiefly responsible for the difference in the stress conditions. Factors which might be considered to influence the stress condition as affected by different firing rates and temperatures include (*a*) physical changes of the body in expansion, elastic, and strength properties; (*b*) changes in similar properties of the glaze and the viscosity-temperature characteristics of the glaze; and (*c*) changes in the properties of the glaze as a result of body-glaze interaction. Some of these conditions offset one another, and an optimum treatment probably exists for any particular glaze and body which would effect the most desirable stress condition possible for that body and glaze.

Schedule No. 4, with one or two exceptions, resulted in a glaze condition similar to that found for No. 2. The cone deformation was greater for No. 2, but the firing time was less. Notable differences in the viscosity-temperature characteristics and in the chemical nature of these glazes might be responsible for these exceptions. From considerable other data not reported here, some of the glazes appeared to be more susceptible than others to change in thermal history. The data for schedule No. 3 were the most inconsistent. This was the shortest firing period. Six out of eight glazes had a lower compression than for schedule No. 4, which had a higher cone temperature and a longer firing time. The variation in glaze stress condition with thermal treatment points out the necessity of using, for comparative data, a standard body and glaze that have the same thermal history or have been fired along with the test specimens.

VII. Conclusions

The conclusions obtained from the data of this investigation indicate that (1) to be able to correlate glaze and body thermal expansions with the resultant glaze stress, the glaze expansion should be taken to its softening point; (2) although individual measurements of glaze and body thermal expansions are valuable in interpreting glaze stress development, these values alone are not always sufficient to establish definitely the resultant glaze stress; (3) both the tuning-fork and ring tests may be used to correlate the glaze stress condition with the effect of the glaze on the properties of a vitreous china body; (4) there is a definite correlation between glaze stress, flexural strength, and thermal endurance of a glazed specimen; an absolute correlation could hardly be expected, but, in general, the glazes tested show that the greater the glaze compression, the higher is the flexural strength and the greater is the thermal endurance; and (5) variation in glaze stress condition with thermal treatment was observed and discussed.

Acknowledgment

The writers wish to acknowledge the advice of G. A. Bole, L. H. Brown, and H. J. Hoffman.

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SECONDARY EXPANSION OF HIGH-ALUMINA REFRACTORIES*

By James L. Hall

Abstract

Several mixtures of raw and calcined diaspore and bauxite with raw and calcined fire clays were prepared and fired at 2700°F. Specimens were refired at higher temperatures, and the linear changes were determined. Bodies composed of high-alumina grog and fire clay expand in the refire, whereas specimens of fire-clay grog that are bonded with ground raw diaspore exhibit shrinkage.

The cause of the secondary expansion and shrinkage of these bodies is discussed.

I. Introduction

A refractory material in use in any high-temperature installation must remain essentially constant in volume. A permanent decrease in brick volume will cause open joints, which admit excess cooling air, allow loss of heat by radiation, and present corners at which spalling and slagging actions start. If permanent volume expansion of the brick manifests itself under load, a distortion or disruption of the furnace structure may also occur.

The phenomenon which takes place when a brick expands in the test for permanent linear change after reheating is known as "secondary expansion" or "after-expansion." There are several types of reactions that may cause this increase in volume. When silica brick are refired above approximately 1400°C., the conversion of tridymite and quartz to cristobalite causes an expansion because the latter material has a lower average density.[1] Brick that show the bleb structure arising from gas expansions in a vitreous body may have a volume increase if they are refired in the appropriate temperature range.[2] Everhart,[3] who subjected many clays to firing-behavior tests, reported that about one half of the nonplastic clays occurring in the Appalachian field are subject to a type of secondary expansion, which is caused by the opening of laminations in the clay during firing.

Another type of reaction which produces secondary expansion has been investigated in the present work. This reaction is confined to those refractories of which one or more of the ingredients is a high-alumina clay, such as diaspore, bauxite, or gibbsite.

(1) Literature Review

Several investigators have examined the firing shrinkage and reheat volume changes of diaspore clay and diaspore-containing refractories. The bauxitic and diasporitic clays exhibit a large shrinkage when they are subjected to high temperatures, and the firing-shrinkage curves show a relatively steep slope up to the softening point. Vachuska and Bole[4] attributed the volume change to an inversion of the diaspore to corundum, but Phelps[5] showed that there is little change in the true density of the mass and that the shrinkage is the result of the shrinkage of the fire-clay bond around the particles of diasporite.

Geller,[6] Harrison,[7] Vachuska and Bole,[4] and Phelps[5] have given data on the reheat-volume changes of various mixtures of diaspore, clay, and calcined kyanite. Shrinkage as well as expansion were encountered in these tests. No theory of the cause of the expansion has been advanced, and any shrinkage encountered has been attributed, in general, to the shrinkage of the diaspore clay.

II. Raw Materials and Method of Investigation

Four clays, namely, Missouri diaspore, Georgia bauxite, Missouri flint, and Georgia kaolin, were selected for the investigation. A thermal analysis of a small sample of each of the first three of these clays was made, utilizing the apparatus and method of Norton.[8] Figure 1, which gives the thermal curves, shows that kaolinite is the only clay mineral present in the Missouri flint clay and that diaspore is the only one present in the Missouri diaspore clay. The Georgia bauxite contains gibbsite with a small amount of kaolinite. Although the Georgia kaolin was not subjected to thermal analysis, it is known to be a pure sedimentary kaolin.

To obtain firing-shrinkage curves, the diaspore, bauxite, and flint clays were crushed through a 4-mesh screen, mixed with an appropriate amount of water, and dry-pressed into briquettes, approximately 3½ by 1 by ¾ in. in size. Sets of four briquettes of each clay were fired at each 100°F. interval from 2200° to 2900° F. The size distribution of the crushed raw clays is

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* Presented at the Forty-Third Annual Meeting, The American Ceramic Society, Baltimore, Md., April 2, 1941 (Refractories Division). Received June 9, 1941.

[1] F. H. Norton, "Thermal Expansion of Refractories," *Jour. Amer. Ceram. Soc.*, **8** [12] 799–815 (1925).

[2] G. A. Loomis, "Porosity and Volume Changes of Clay Fire Brick at Furnace Temperatures," *Nat. Bur. Stand. Tech. Paper*, No. 159, 29 pp. (April 26, 1920); *Ceram. Abs.* in *Jour. Amer. Ceram. Soc.*, **3** [7] 581–82 (1920).

[3] J. O. Everhart, "Secondary Expansion in Refractory Clays," *Jour. Amer. Ceram. Soc.*, **20** [11] 353–59 (1937).

[4] E. J. Vachuska and G. A. Bole, "Notes on Kyanite and Diaspore Refractories," *Jour. Amer. Ceram. Soc.*, **10** [10] 761–73 (1927).

[5] S. M. Phelps, "Study of the Shrinkage of Diaspore Clays, I–II," *ibid.*, **9** [10] 659–66 (1926); **15** [2] 96–106 (1932).

[6] R. F. Geller, "Laboratory Testing of Aluminous Refractories," *ibid.*, **7** [9] 663–69 (1924).

[7] H. C. Harrison, "Kyanite-Clay Refractories, I," *ibid.*, **9** [5] 257–71 (1926).

[8] F. H. Norton, "Critical Study of the Differential Thermal Method for Identification of Clay Minerals," *ibid.*, **22** [2] 54–63 (1939); see also F. H. Norton, "Analysis of High-Alumina Clays by the Thermal Method," *ibid.*, **23** [9] 281–82 (1940).

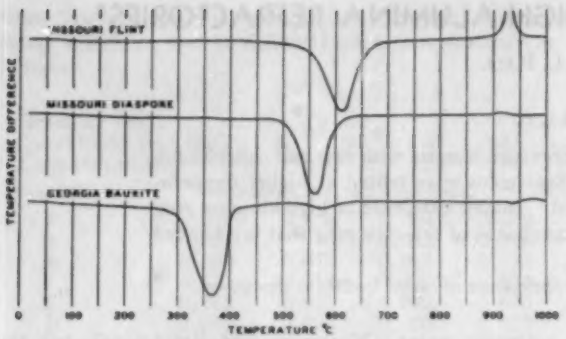

FIG. 1.—Thermal-analysis curves.

TABLE I

GRAIN-SIZE DISTRIBUTIONS OF RAW CLAYS CRUSHED THROUGH 4-MESH

Mesh size	Mo. diaspore (%)	Ga. bauxite (%)	Mo. flint (%)
4–8	21.0	24.0	29.8
8–14	23.0	27.5	27.7
14–35	21.6	30.9	27.2
35–65	10.8	9.0	9.1
65–100	7.2	3.1	2.8
−100	16.4	5.4	3.5
Total	100.0	99.9	100.1

given in Table I, and Fig. 2 shows the firing-shrinkage curves.

The firing, in general, was started by heating slowly overnight with a large Méker burner to about 600°F. This burner was replaced in the morning with a blowpipe, and the temperature was raised slowly through the dehydration range to red heat. A premix burner was then started, and the temperature was raised at a rate of 7° to 10°F. per minute until the firing temperature was reached.

Although the temperature of the kiln was held to ±10°F., it deviated ±25°F. occasionally for short periods of time. After holding the kiln at the desired temperature for 5 hr., the gas was shut off, and the kiln was allowed to cool to room temperature.

The length of each of the specimens before and after firing was measured with a vernier caliper, which could be read to a precision of 0.01 cm. Three measurements on each specimen were averaged to give the length of each specimen, and the values of the four specimens were averaged in most cases to give the length for any one temperature treatment. The percentage of change in length, based on the original length, was then calculated and plotted.

Reheat linear changes in high-temperature firing were determined for a number of specimens in which grog of one clay was bonded with another clay.

The grog was prepared in three ways, as follows: (1) The clays were ground so that all of the particles passed through a 100-mesh screen; they were mixed well with a suitable amount of water, dry-pressed into

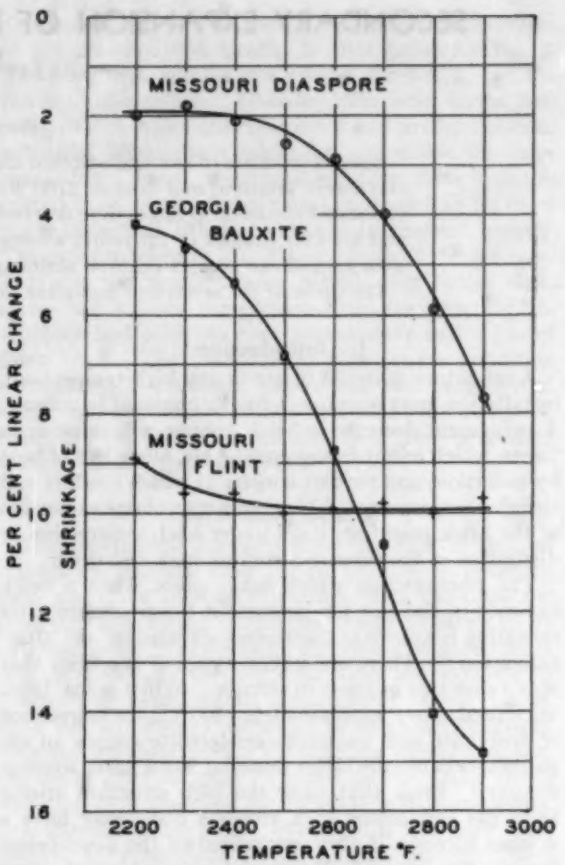

FIG. 2.—Firing-shrinkage curves.

brick, and calcined at 3000°F. for 5 hr.; (2) the clays were crushed through 16-mesh, dry-pressed, and calcined at 2900°F. for 5 hr.; and (3) the clays were calcined at 2900°F. in their original lump size. These fired materials were crushed, ground, and sized to give the grain-size distribution shown in Table II; abraded iron from the crushers was removed from all of the fractions with a hand magnet.

TABLE II

GRAIN-SIZE DISTRIBUTION OF GROG

Mesh size	(%)	Mesh size	(%)
4–8	35	35–65	4
8–14	15	65–100	20
14–35	6	−100	20

Various mixtures of grogs, flint clay, and bond clay were prepared as shown in Table III. The components were mixed and blended with a suitable amount of water and were dry-pressed into briquettes as in the tests on firing behavior.

All of the briquettes were fired initially at 2700°F. for 5 hr., and a set of four of each series was refired at 2800°, 2900°, and 3000°F. for 5 hr., using the same firing schedule as previously described.

TABLE III

BODIES COMBINING TWO CLAYS

	Clay	Body No. 1	2	3	4	5	6	7	8	9	10	11	12
(1)	Mo. diaspore raw							27.9					
(2)	" " grog	75	50	50	50								
(3)	" " "					75							
(4)	" " "						72.1						
(5)	Ga. bauxite grog								75	50	50	50	
(6)	" " "												75
(7)	Mo. flint raw			50							50		
(8)	" " grog				50							50	
(9)	Ga. kaolin raw	25				25	27.9		25				25
(10)	" " grog		50					72.1		50			

(1) Ground in ball mill to pass 100-mesh.
(3) Crushed through 16-mesh, briquetted, calcined at 2900°F. for 5 hr.
(2) Calcined in original lump size at 2900°F. for 5 hr.
(4) Ground in ball mill to pass 100-mesh, briquetted, calcined at 3000°F. for 5 hr.
(5) Crushed through 16-mesh, briquetted, calcined at 2900°F. for 5 hr.
(6) Calcined in original lump size at 2900°F. for 5 hr.
(7) Crushed and sieved to give grain-size analysis in Table II.
(8) Calcined in original lump size at 2900°F. for 5 hr.
(9) Air-floated.
(10) Air-floated material briquetted, calcined at 3000°F. for 5 hr.

The apparent porosities of the specimens were determined, using the A.S.T.M. standard water-absorption method, C20–33. The true density of several of the specimens was determined by the pycnometer method, using tetrahydronaphthalene (tetralin) as the liquid. With these data, the true porosities of the specimens were calculated.

Thin sections of several of the specimens were prepared for study under the microscope, and X-ray diffraction patterns of certain portions of some of the specimens were also made. For the X-ray analysis, well-sampled portions of the specimens were crushed and ground in an agate mortar, and small cylinders of the material, about $^1/_2$ mm. in diameter, were extruded from a glass capillary tube. These specimens were placed in the center of a Debye-Scherrer camera, 57.3 mm. in diameter, and exposed to CuKα radiation for about $2^1/_2$ to $3^1/_2$ hours.

III. Test Results and Discussion

The changes in length in the initial fire at 2700°F. and the porosities of the specimens are listed in Table IV.

TABLE IV

LINEAR CHANGES AND POROSITIES OF BODIES FIRED AT 2700°F.

Body No.	Linear change* (%)	Porosity† (%)	Body No.	Linear change* (%)	Porosity† (%)
1	+0.4	*31.0*	7	−1.0	20.6
2	+1.2	*35.7*	8	−0.5	27.4
3	+1.1	*34.5*	9	+0.6	34.1
4	+1.0	*35.9*	10	+1.6	*36.2*
5	+0.5	*32.3*	11	+0.4	31.2
6	+0.3	23.7	12	−0.4	25.5

* Based on unfired length; minus (−) sign denotes shrinkage; plus (+) sign, expansion.
† Values in italics are true porosity; others are apparent porosity.

The results of the refiring treatments of the specimens containing diaspore are plotted in Fig. 3. All of the diaspore-grog specimens expand in the refire; bodies Nos. 1, 3, and 6, containing raw clay as bond, change to a greater extent than those composed of two grogs. The secondary expansion, in general, increases practically linearly with temperature. Body No. 7, containing 72.1% of kaolin grog bonded with 27.9% of raw diaspore, exhibited secondary shrinkage which

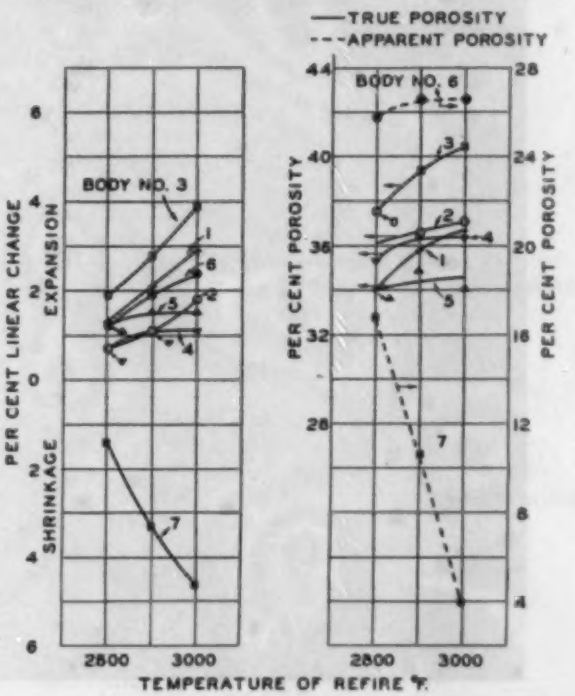

FIG. 3.—Changes in length and porosity of bodies containing Missouri diaspore.

was approximately proportional to the temperature of refire. From the true porosity curves of Fig. 3, the expansion is seen to be almost directly proportional to the change in porosity.

The refire changes in length and in the porosity of the specimens containing bauxite are plotted in Fig. 4.

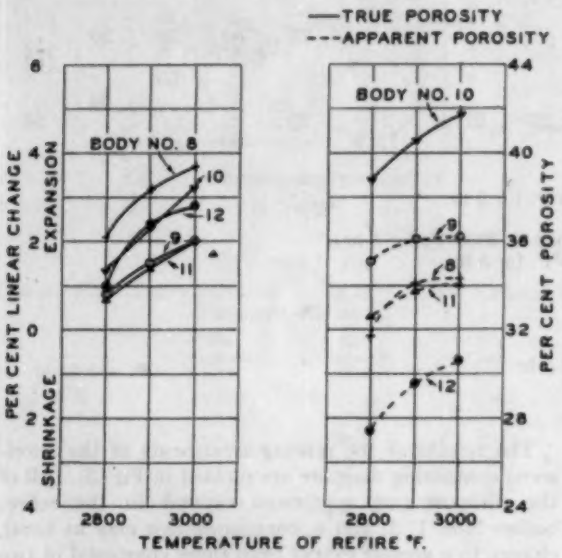

FIG. 4.—Changes in length and porosity of bodies containing Georgia bauxite.

As in the case of the diaspore grog, all of the bauxite-grog briquettes expanded in the refire, and the specimens containing raw clays increased to a greater extent than those composed of two grogs.

The reheat curves show that secondary expansion has taken place in bodies prepared with grog of widely different mechanical properties. Grogs of high-alumina clays from two different sources induced secondary expansion. The grog, which was made by crushing the clay through a 16-mesh screen and firing at 2900°F., was not well consolidated; it appeared to have a relatively high porosity, and the lumps could be broken apart easily with the fingers. The grog, produced by firing briquettes of clay at 3000°F., was vitrified, very hard, and difficult to crush. It is thus apparent that the preparation treatment of the grog has little qualitative effect on secondary expansion although it has considerable influence quantitatively.

The type of fire clay used in the body is likewise unimportant. Two fire clays, one a flint and the other a plastic, both raw and calcined, were incorporated with high-alumina grog in bodies that exhibited secondary expansion. It is significant that secondary expansion occurs when high-alumina grog is used, whereas kaolin grog bonded with raw diaspore clay exhibits shrinkage.

Figures 5 and 6 show thin sections of specimens made by bonding diaspore grog with raw kaolin (body No. 6); Fig. 5 shows a specimen fired at 2700°F. with no refire, and Fig. 6 pictures a specimen fired at 2700°F. and refired at 3000°F. These photomicrographs show

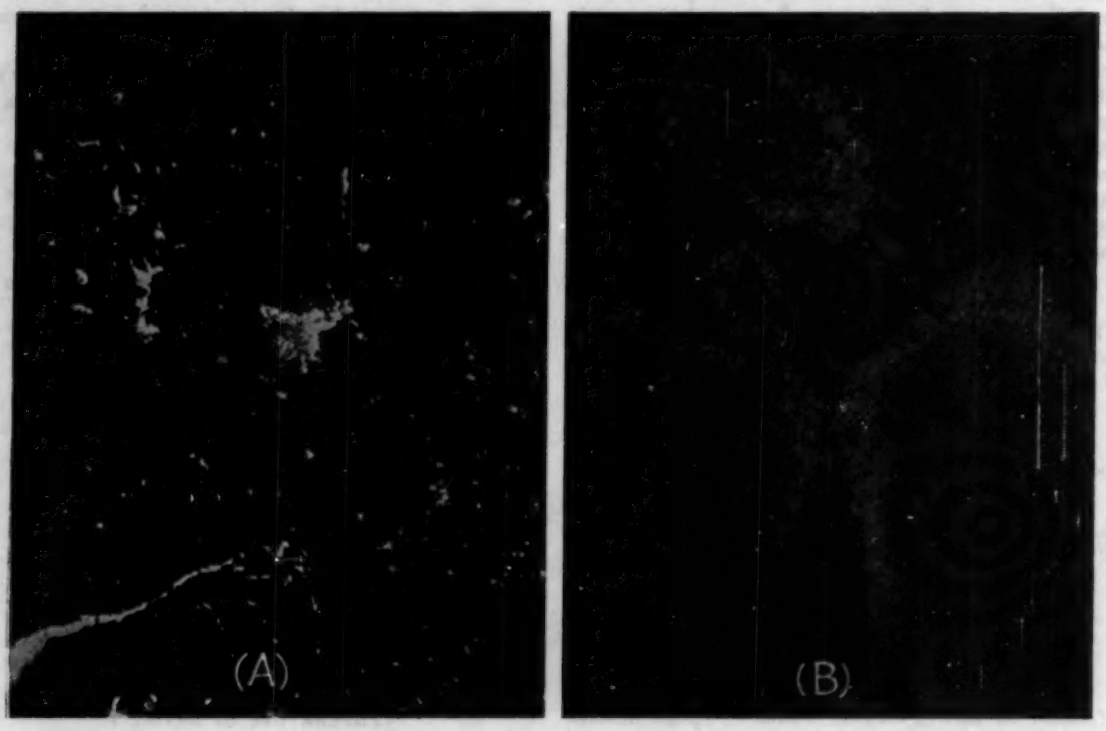

FIG. 5.—Thin sections of diaspore-grog specimens bonded with raw kaolin; fired at 2700°F. with no refire; (*A*) ordinary light, ×15.6; (*B*) crossed Nicols, ×15.6.

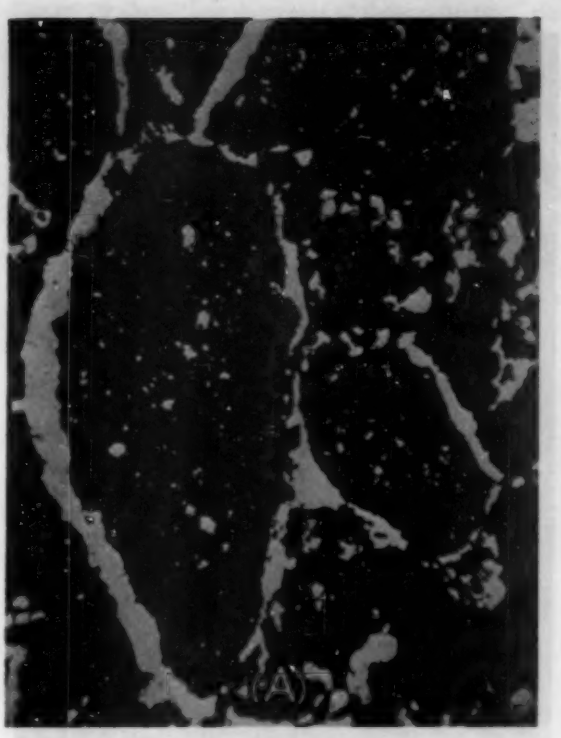

FIG. 6.—Same body shown in Fig. 5 but fired at 2700°F. and refired at 3000°F.; (*A*) ordinary light, ×15.6; (*B*) crossed Nicols, ×15.6.

the effect of the heat-treatment on the various components of the body. Around each grog grain occurs a rim of increased reaction in which crystals become more and more developed as the temperature of refire is increased. Further effect of heat-treatment at higher temperatures occurs in the bond between the diaspore grains. In the specimen fired at 2700°F., the bond has only begun to shrink and the body is relatively dense. When this specimen is refired, the bond undergoes further shrinkage and appears to attach itself to the grog grains and break apart, agglomerate around the grains, and leave large pore spaces.

The crystals were too small to identify petrographically even after the highest temperature-treatment. The X-ray method was used, and powder-diffraction patterns were made of the outside ring and of the inside portions of diaspore-grog grains from a specimen refired at 3000°F. Line drawings of the patterns are given

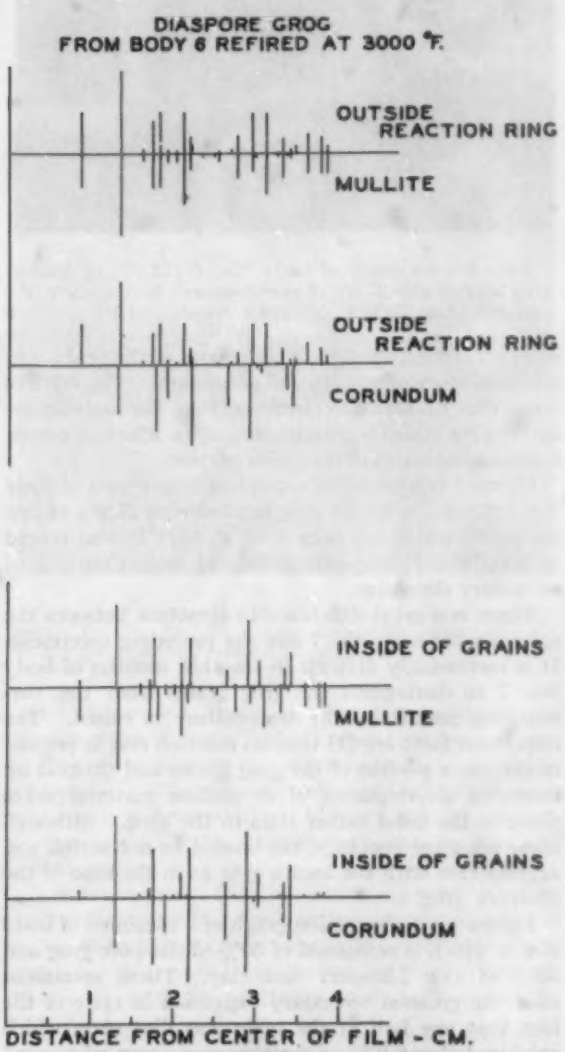

FIG. 7.—Powder diffraction patterns of specimens showing mixture of mullite and corundum.

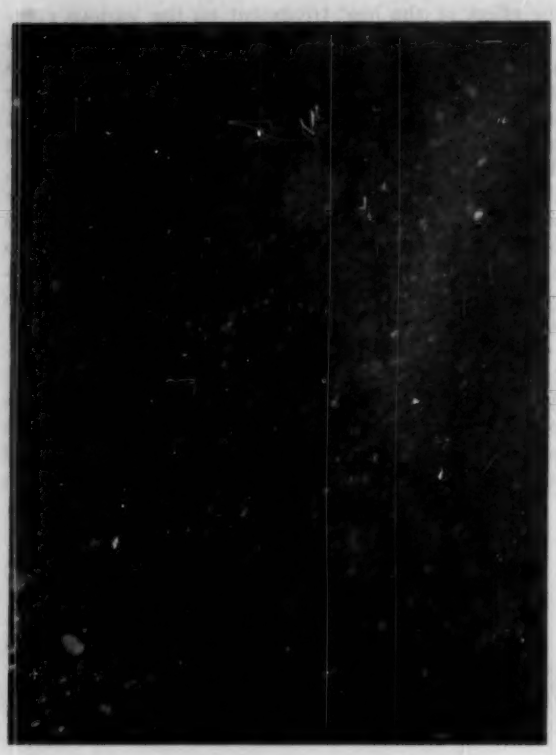

FIG. 8.—Specimen of body No. 7 (72.1% of kaolin grog bonded with 27.9% of raw diaspore), fired at 2700°F. and refired at 3000°F.; crossed Nicols, ×15.6.

FIG. 9.—Specimen of body No. 3 (50% of diaspore grog and 50% of raw Missouri flint clay); crossed Nicols, ×15.6.

in Fig. 7, which show that both parts of the grain contain a mixture of mullite and corundum. The relative intensities of the lines indicate that the outside reaction ring consists mainly of mullite whereas corundum predominates in the inside portion.

Figure 8 is a photomicrograph of a specimen of body No. 7 (72.1% of kaolin grog bonded with 27.9% of raw diaspore), which has been fired at 2700°F. and refired at 3000°F. This specimen showed more than 4% of secondary shrinkage.

There is a great difference in structure between the specimens of body No. 7 and the preceding specimens. It is increasingly difficult in the thin sections of body No. 7 to distinguish the grog grains from the surrounding matrix as the temperature is raised. The important facts are (1) that no reaction ring is present in the outer portion of the grog grains and (2) that an increased development of crystalline material takes place in the bond rather than in the grog. Although there are some openings, the bond does not shrink and agglomerate with the kaolin grog as in the case of the diaspore grog.

Figure 9 is a photomicrograph of a specimen of body No. 3, which is composed of 50% of diaspore grog and 50% of raw Missouri flint clay. These specimens gave the greatest secondary expansion in spite of the fact that one half of the body was flint clay, which exhibited about 10% of shrinkage on firing when used alone (see Fig. 2). The photomicrograph shows the effect of this shrinkage. The large flint-clay grains have contracted away from the rest of the body, leaving an open space around each grain. These large flint-clay grains are held loosely and may easily be picked out of a fractured specimen with the fingers or with a knife blade. The reaction in the diaspore-grog grains is not so apparent as in body No. 6 (Fig. 5) because the grog in the latter case was well consolidated and vitrified, whereas that of body No. 3 was porous and easily broken. In this photomicrograph, however, a margin of increased reaction is revealed in the somewhat obscure diaspore particles. Because of the large shrinkage of the flint grains, the expansion of the specimens was obviously caused by some reaction in the diaspore grains.

The photomicrographs show (1) that in the bodies that exhibit secondary expansion, a ring of mullite development, which increases in refire, appears in the outer portion of the diaspore-grog grains bonded with fire clay and (2) that in bodies composed of kaolin grog bonded with raw diaspore, the increased mullite development is in the bond, and these bodies show secondary shrinkage. It is concluded from these facts that the changes are the result of a transfer of silica from the kaolin to the diaspore.

To show the change in the free silica content of the kaolin, X-ray diffraction patterns were made of kaolin-grog grains, some of which had been incorporated into specimens with diaspore grog whereas others were not.

Figure 10 shows line diagrams of these patterns; Fig. 10 (*A*) is the pattern of kaolin-grog grains which had been calcined at a temperature near the melting point; Fig. 10 (*B*) is the pattern of kaolin-grog grains from body No. 2, which had been fired at 2700°F. and refired at 3000°F. The strong line of cristobalite is evident in Fig. 10 (*A*) but is absent in Fig. 10 (*B*), which indicates that the silica in excess of the mullite composition in the original kaolin grog has either been carried away during the firing treatment of the specimen or has been dissolved in the glassy phase. Because the pattern of the highly calcined grog still contained the cristobalite line, the former reaction probably occurred, that is, the excess silica was removed from the kaolin grog.

Norton[9] has investigated the effect of the amount of bond on the firing shrinkage of brick made with grog. The results show that grog alone or bonded up to the point at which the pores are completely filled has a small but constant shrinkage which increases progressively with more bond to a maximum at 100% of bond. This indicates that up to the point at which the bond fills the pores in the grog mixture, the grog particles determine the structure of the mass, and volume changes in the grog particles will be reflected in changes of the bulk volume.

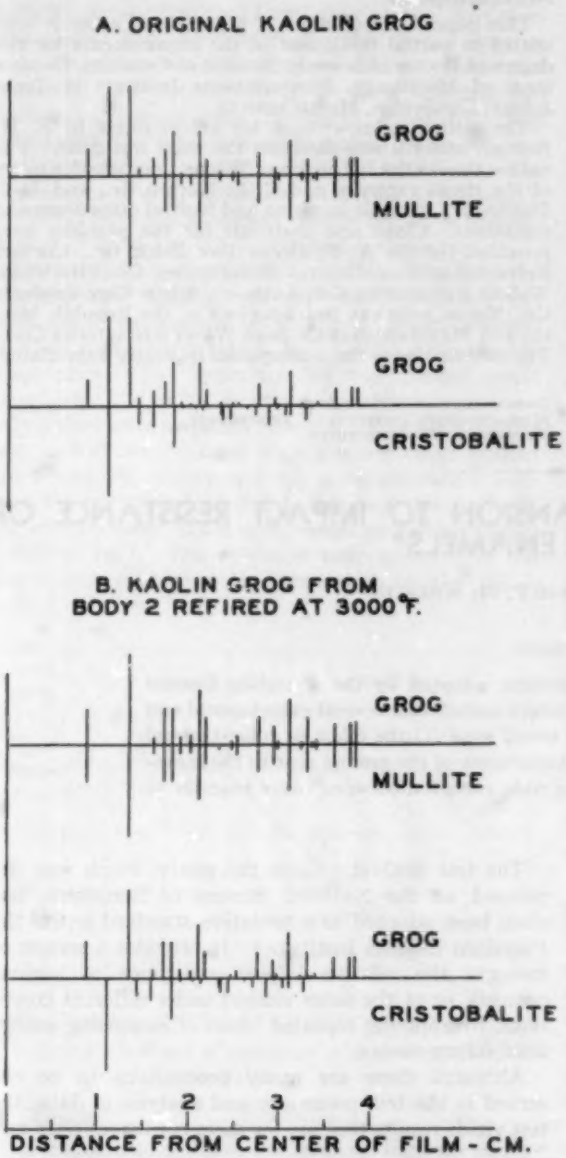

FIG. 10.—Diagrams of X-ray diffraction patterns; kaolin-grog grains, *A*, calcined near melting point; *B*, from body bonded with diaspore grog.

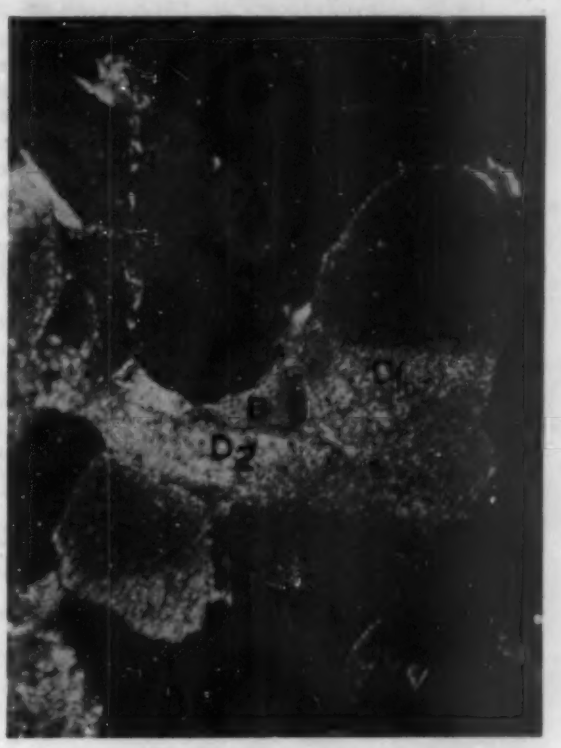

FIG. 11.—Thin section of fired body; *B*, Bakelite resin area; D_1, D_2, and D_3 grains, originally diaspore; *K*, kaolin-grog grains; crossed Nicols, ×15.6.

It is concluded, therefore, that the secondary expansion of the bodies of high-alumina grog bonded with fire clay is caused by the increase in the size of the grog grains. This volume increase of the high-alumina grog grains is brought about by silica transferred from the fire clay, which reacts with corundum in the grog to form mullite.

It is not apparent from the preceding work whether the transfer of silica is through the vapor or the liquid phase. The photomicrographs in Fig. 6 show that the large grog grains are held in place by relatively small columns of matrix, and there are void spaces around the

[9] F. H. Norton, Modern Treatise on Refractories, pp. 227–28. McGraw-Hill Book Co., Inc., New York, 1931. 600 pp.; *Ceram. Abs.*, **11** [1] 40 (1932).

greater part of the circumference of each grain. The transfer of silica then could take place either by diffusion through the glassy matrix or by volatilization and transfer across the void spaces. If the former reaction occurs, the reaction edge would be expected to be thicker and the crystals developed better in those portions of the grog grain immediately adjacent to the point at which there is contact between the grog grain and the matrix. If vaporization takes place, the thickness of the reaction edge of each grog grain should be nearly uniform around the entire circumference.

In Figs. 5, 6, and 9, this effect has been obscured by the good distribution of the fine fractions of the fire clays around the larger grog particles. To determine the mechanism of the transfer, specimens were made of equal amounts of diaspore-grog and kaolin-grog grains which passed through an 8-mesh screen and were retained on a 14-mesh screen. These grog grains were mixed, bonded with dextrin, and fired for 5 hr. at 3000°F. The specimens exhibited 5.1% of permanent expansion in the firing operation. Figure 11 is a photomicrograph of a thin section of the fired body. The light area marked *B* is Bakelite resin with which the specimen was impregnated for thin sectioning. Grains, originally diaspore grog, are marked D_1, D_2, and D_3, and kaolin-grog grains are indicated by *K*.

The transfer of silica obviously takes place by movement through the liquid phase. The lower half of the grain, D_1, is in contact with two kaolin-grog grains, and it is filled with small mullite crystals, whereas the upper half of D_1 shows normal mullite development. Both extremities of D_2 are in contact with kaolin grog and the grain appears to be completely saturated with mullite. It is also significant that there is no reaction ring around those diaspore grains that are not in contact with kaolin.

IV. Conclusions

Permanent expansion in refired bodies that are compounded of high-alumina grog bonded with fire clay is caused by the volume increase of the high-alumina grog grains. These expand because of the influx of silica from the fire clay through the liquid phase, the silica combining with the corundum in the high-alumina grog to form mullite.

Acknowledgment

This paper is an abstract of a portion of a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Science, Division of Ceramics, Department of Metallurgy, Massachusetts Institute of Technology, Cambridge, Massachusetts.

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RELATION OF COEFFICIENT OF EXPANSION TO IMPACT RESISTANCE OF PORCELAIN ENAMELS*

By R. L. Fellows and P. M. Wheeler

Abstract

The tentative standard impact test procedure, adopted by the Porcelain Enamel Institute, was used to test and compare cylinders coated with several experimental and commercial enamels. The important facts noted were (1) the effect of cubic thermal expansion on the impact resistance, (2) the importance of the ground coat to the resistance of any one cover enamel, and (3) the wide variation between cover enamels in resistance to impact.

I. Introduction

One of the most common and annoying defects currently encountered in the enamel industry is the chipping caused by mechanical impact. Failure by impact has long been understood to represent only a portion of the chipping problem, and there are many limitations on the means of testing for such failure. Many tests have been discussed, proposed, and used, and the published reports have included data that vary over a rather wide range.

The test method used in this study, which was developed at the National Bureau of Standards, has since been adopted as a tentative standard test of the Porcelain Enamel Institute.[1] It provides a means to measure the relative impact resistance of various enamels, or of the same enamel under different conditions, by applying repeated blows of increasing energy until failure occurs.

Although there are many precautions to be observed in the test procedure and analysis of data, the test yields results that are far more consistent than any

* Presented at the Forty-Third Annual Meeting, The American Ceramic Society, Baltimore, Md., April 1, 1941 (Enamel Division). Received April 2, 1941.

[1] "Impact Test for Laboratory Specimens of Porcelain Enameled Sheet Iron and Steel," *Porcelain Enamel Inst. Tentative Standard Bull.* (August, 1940).

from tests used in the past. The present study not only presents interesting and useful data but may also help to establish the merit of the test method used.

II. Test Method

The standard apparatus, specimens, and procedure as recommended[1] were used. The cylindrical specimens were enameled with one coat of ground coat and two coats of white finish enamel as specified.

III. Variation in Ground Coat

(1) Procedure

This part of the experiment was confined to the study of the effect of variations in the ground coat, using the same cover coat for all specimens. Five steel ground-coat frits were developed that would cover a wide range in cubic thermal-expansion values and yet would have approximately the same hardness and maturing characteristics. Each of these frits was milled with the same soft ground-coat frit in the proportion of 80% of hard frit and 20% of soft frit. The percentages of mill additions were clay 7, feldspar 3, and borax ½. Each enamel was milled to a fineness of 8 to 10% by the P.E.I. standard fineness test.

The coefficient of expansion was determined by the interferometer method, and the values given are the mean cubic expansions of the fused milled enamels between room temperature and 300°C. above room temperature. The expansion of the ground coats varied from 274 to 307 as shown in Table I.

Cylinders were prepared in sets of six for each ground coat, and all were coated with a white cover enamel milled with 7% of clay and 2% of opacifier to a fineness of 5 to 7% by the P.E.I. standard fineness test. The white enamel had a cubic coefficient of expansion of 315 × 10^{-7}. The cylinders were tested, and the results were calculated for comparison by the P.E.I. method.

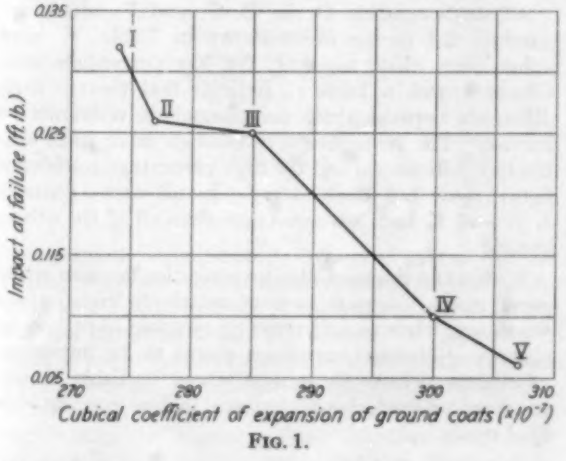

FIG. 1.

(2) Results

The statistical results of the tests on each set of six cylinders are shown in Table I and plotted in Fig. 1 along with the corresponding cubic thermal-expansion values.

The significance of a difference between any two of these mean values is expressed in terms of percentage confidence. This figure indicates whether the difference in mean values is due to a systematic difference between the two enamels or only to variations in experimental procedure. The percentage confidence figures for the ten possible comparisons in the investigation are shown in Table II.

TABLE I

Temp. 80°; relative humidity 38%

Ground-coat enamel No.	Cubic thermal expansion × 10^{-7}	Impact blow No. at failure	Energy at failure (ft.-lb.)
I	274	10.55 ± 0.94	0.132 ± 0.012
II	277	10.01 ± 0.72	0.126 ± 0.009
III	285	10.00 ± 0.53	0.125 ± 0.007
IV	300	8.80 ± 0.69	0.110 ± 0.009
V	307	8.47 ± 0.35	0.106 ± 0.004

TABLE II

Ground-coat comparison	Confidence (%)
I–II	Below 90.0
I–III	" "
I–IV	97.0
I–V	99.0
II–III	Below 90.0
II–IV	98.0
II–V	99.0
III–IV	"
III–V	"
IV–V	Below 90.0

The basis of classification for percentage confidence figures as recommended by the P.E.I. is as follows: 99% or higher, highly significant; 95 to 99%, significant; 90 to 95%, indicative; and below 90%, not recommended for consideration.

Four of the ten possible comparisons in the experiment fall in the highly significant classification and two are classed as significant. Although the other four are lower than is recommended for consideration, the trend of the entire group is established and gives satisfactory evidence that variations in the ground-coat enamel result in important changes in resistance to impact blows.

IV. Variation in Cover Coat

(1) Procedure

A study of the impact resistance of several cover enamels was made. To secure a representative sample, eleven commercial enamels were selected for study; these were applied over three different ground coats in order to correlate this part of the study with the preceding part. The ground coats, Nos. I, III, and V (from section III), represented a range in mean values of impact, and their use should aid in verification of the results of section III. Three sets of six specimens each (one set for each ground coat) were prepared from each cover enamel. All of the cover enamels were milled with 7% of clay and 2% of opacifier to a fineness

TABLE III

Temp. 84°; relative humidity 43%

Ground-coat group	Cover enamel No.	Cover enamel Type	Cubic thermal expansion of cover enamel $\times 10^{-7}$	Impact blow No. at failure	Energy at failure (ft.-lb.)
I (expansion = 274)	A	Superopaque	325	11.09 ± 0.73	0.139 ± 0.009
	B	Zircon opacified	326	10.58 ± 0.98	0.132 ± 0.012
	C	" "	305	10.37 ± 0.57	0.130 ± 0.007
	D	Superopaque	303	9.89 ± 0.35	0.124 ± 0.004
	E	"	323	9.60 ± 0.48	0.120 ± 0.006
	F	"	331	9.37 ± 0.65	0.117 ± 0.008
	G	Clear glass	303	9.21 ± 0.78	0.115 ± 0.009
	H	Acid-resisting mat	313	8.40 ± 0.32	0.105 ± 0.004
	I	Acid resisting	290	8.31 ± 0.71	0.104 ± 0.009
	J	" "	293	8.21 ± 0.54	0.103 ± 0.007
	K	" "	265	7.64 ± 0.48	0.096 ± 0.006
III (expansion = 285)	A	Superopaque	325	9.73 ± 0.38	0.122 ± 0.005
	B	Zircon opacified	326	8.00 ± 0.40	0.100 ± 0.005
	D	Superopaque	303	7.94 ± 0.49	0.099 ± 0.006
	E	"	323	7.73 ± 0.15	0.097 ± 0.002
	C	Zircon opacified	305	7.69 ± 0.47	0.096 ± 0.006
	G	Clear glass	303	7.60 ± 0.43	0.095 ± 0.005
	F	Superopaque	331	7.52 ± 0.71	0.094 ± 0.009
	H	Acid-resisting mat	313	7.01 ± 0.25	0.088 ± 0.003
	J	Acid resisting	293	6.70 ± 0.36	0.084 ± 0.005
	I	" "	290	6.61 ± 0.41	0.083 ± 0.005
	K	" "	265	6.45 ± 0.51	0.081 ± 0.006
V (expansion = 307)	A	Superopaque	325	7.81 ± 0.24	0.098 ± 0.003
	D	"	303	7.05 ± 0.34	0.088 ± 0.004
	E	"	323	6.56 ± 0.15	0.082 ± 0.002
	F	"	331	6.47 ± 0.14	0.081 ± 0.002
	G	Clear glass	303	6.32 ± 0.43	0.079 ± 0.005
	C	Zircon opacified	305	6.31 ± 0.13	0.079 ± 0.002
	H	Acid-resisting mat	313	6.26 ± 0.22	0.078 ± 0.003
	B	Zircon opacified	326	6.24 ± 0.29	0.078 ± 0.004
	J	Acid resisting	293	5.96 ± 0.24	0.074 ± 0.003
	I	" "	290	5.66 ± 0.37	0.071 ± 0.005
	K	" "	265	5.40 ± 0.20	0.067 ± 0.002

of 5 to 7% according to the P.E.I. fineness test, and the necessary setup agents were used as required. The expansion data were determined by the interferometer method on the fused milled enamel (see section III). All were tested, and the results were computed by the same method as described in that section.

(2) Results

The tabulation of all of the values and pertinent data is included in Table III.

The analysis of the impact values to show the significance of any difference between sets of specimens is made from the percentage confidence figures. These were computed for all possible comparisons and are shown in Table IV.

The large number of comparisons makes the analysis of these data difficult. A study, however, of the impact values of each group in Table III and the percentage confidence values from Table IV permits the rating of the cover-coat enamels tested as shown in descending order of impact resistance in Table V.

These values show a distinct difference between cover enamels in resistance to impact. The data in Tables III and IV show that enamel A is definitely better than all of the other enamels tested. This conclusion is reached because, in the three ground-coat groups, enamel A had the highest mean impact value, that is, more foot-pounds of energy were necessary to cause chipping than for any other enamel and there was such a high percentage confidence that this difference was significant.

Although enamels D, B, E, C, and F, which apparently fall in the order shown in Table V, have values very close together, the low percentage confidence figures in Table IV indicate that there is little difference between these five enamels in resistance to impact. The remaining five enamels have more distinctive differences, and the high percentage confidence figures bear out their rating. In all cases, enamels I, J, and K had less resistance than all of the others tested.

Within the limits of this investigation, regular white cover enamels appear to have relatively high impact resistance, whereas acid-resisting enamels have low resistance. Thermal expansion seems to be important as evidenced from the general trend in Table V, but the composition and other physical factors enter into the final result.

V. Discussion

The results of this investigation seem to indicate several important factors that merit consideration in a study of the chipping problem.

TABLE IV

PERCENTAGE CONFIDENCE OF COVER-COAT COMPARISONS*

Cover-coat comparison	Ground-coat No. I	III	V	Cover-coat comparison	Ground-coat No. I	III	V
A–B	–	99	99	D–E	–	–	98
A–C	90	"	"	D–F	–	–	99
A–D	98	"	"	D–G	90	–	"
A–E	99	"	"	D–H	99	99	"
A–F	"	"	"	D–I	"	"	"
A–G	"	"	"	D–J	"	"	"
A–H	"	"	"	D–K	"	"	"
A–I	"	"	"				
A–J	"	"	"	E–F	–	–	–
A–K	"	"	"	E–G	–	–	–
				E–H	99	99	97
B–C	–	–	–	E–I	"	"	99
B–D	–	–	99	E–J	"	"	"
B–E	90	–	95	E–K	"	"	"
B–F	93	–	–				
B–G	96	–	–	F–G	–	–	–
B–H	99	99	–	F–H	98	–	90
B–I	"	"	97	F–I	96	99	99
B–J	"	"	90	F–J	99	95	93
B–K	"	"	99	F–K	"	97	99
C–D	–	–	99	G–H	94	97	–
C–E	95	–	97	G–I	92	99	98
C–F	95	–	92	G–J	96	"	90
C–G	97	–	–	G–K	99	"	99
C–H	99	97	–				
C–I	"	99	99	H–I	–	91	98
C–J	"	"	98	H–J	–	–	93
C–K	"	"	99	H–K	98	94	99
				I–J	–	–	–
				I–K	90	–	–
				J–K	90	–	99

* Dash (–) indicates figure below 90%.

TABLE V

Cover enamel	Type of cover enamel	Cubic thermal expansion $\times 10^{-7}$
A	Superopaque	325
D	"	303
B	Zircon opacified	326
E	Superopaque	323
C	Zircon opacified	305
F	Superopaque	331
G	Clear glass	303
H	Acid-resisting mat	313
J	Acid resisting	293
I	" "	290
K	" "	265

As pointed out by Smith,[2] chipping of enamel may be divided into two classes, namely, the type that originates at the outer surface of the enamel and the type that has its origin within the enamel. Chipping as a result of impact is not included in either of the classifications because, as Smith states, chips caused by impact sometimes start at the surface and sometimes start within the enamel. There are also other complicating factors that prevent a definite classification. All of the chips were oval in shape, with a smooth surface of ground coat exposed. A small round point of enamel also remained intact at the point of impact with the oval portion chipped from around the point.

Many factors contribute to the impact resistance of porcelain enamel, and among the more important of these are adherence, hardness, bubble structure, thickness, thermal expansion, and elasticity. In this investigation, the ground-coat adherence and hardness were kept constant, and the thickness of both the ground coat and the cover coat was controlled so as to produce a minimum of variation. Evidently thermal expansion, elasticity, and bubble structure of both the cover coat and ground coat and the hardness of the cover coat are important.

The only readily measurable factor that was varied in the ground coat was the thermal expansion, and a definite relation seems to exist for this particular group of ground coats. The chipping resistance increases as the cubic thermal expansion of the ground coat is lowered. The other important factor to consider is the bubble structure of the ground coat. In these enamels, the one having a low expansion and high impact resistance also had a dense structure with only a limited number of bubbles present, and this number increased with the increase of expansion in the ground-coat enamels. This evidence leads to the belief that a dense ground coat, with only a small number of bubbles and flaws, contributes to impact resistance.

The impact resistance in the cover coats does not seem to be as definitely related to thermal expansion. The enamels with high- and medium-expansion values, however, are evidently better than those with low expansion. Elasticity, as mentioned by Parmelee,[3] probably is an important contributing factor to the resistance to impact of cover enamels. It is known also that the acid-resisting enamels, which have poor impact resistance, are more dense and have less bubble structure than the other cover enamels tested. As noted in the first part of this study, the resistance of each set of specimens increased as the expansion of the ground coat was lowered.

Impact resistance is a combination of many factors, some aiding and some detracting from this property of the enamel. More attention in the past has been given to cover-coat studies than to the ground coat. Table III shows that the impact resistance of any one cover coat may be materially changed by a variation in the ground coat.

VI. Conclusions

(1) The impact resistance of porcelain enamels apparently depends on many factors, all of which affect the final value, and the physical properties of the ground coat are evidently an important factor in the impact strength of porcelain enamel.

(2) The impact strength of enamelware seems to increase as the cubic thermal expansion of the ground coat is lowered.

[2] P. L. Smith, "Measuring Chipping Resistance of Enamels," *Proc. Porcelain Enamel Inst. Forum, Fourth Forum, Oct., 1939*, pp. 155–62; *Ceram. Abs.*, **19** [7] 156 (1940).

[3] L. D. Fetterolf and C. W. Parmelee, "Effects of Soda, Barium, and Zinc on Elasticity and Thermal Expansion Coefficients of Glass," *Jour. Amer. Ceram. Soc.*, **12** [3] 193–216 (1929).

(3) The impact strength of enamelware apparently depends somewhat on the bubble structure of the ground coat; a dense ground coat with relatively few bubbles seems to impart a higher impact strength than one with many bubbles and flaws.

(4) The impact strength of enamelware does not directly follow the cubic thermal-expansion values of the cover coats. Low-expansion cover coats, in general, have poor resistance to impact, and high-expansion cover coats have good resistance.

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DEVELOPMENT OF OPACITY IN ZIRCONIA ENAMELS*

BY BURNHAM W. KING, JR., AND ANDREW I. ANDREWS

ABSTRACT

Opaque zirconia-bearing enamels are divided into two general types, namely, those whose opacity is due (1) to the undissolved residue of the zirconia added in the raw batch and (2) to the crystallization of a zirconia compound during firing. These enamels are described and illustrated. The quantity, identity, and appearance of the materials causing opacity in representative samples of each group of enamels are given.

I. Theory of Development of Opacity

Opaque enamels consist of a clear glass matrix in which particles are suspended which have a different refractive index than the surrounding medium. Owing to this difference in optical properties, the light which strikes the particles is scattered. If a great number of particles is present, a large fraction of the incident light will be scattered and will eventually emerge from the surface of the enamel as diffuse reflection.

The size of the single particles giving the highest reflectance varies from 0.2 to 0.3 μ, depending on the wave length of the incident light. Figure 1 was taken from transmission data obtained by Stutz[1] for zinc oxide particles suspended in water. The data are plotted as one minus the transmission coefficient, inasmuch as these values would equal the reflectance if there were no absorption of light.

In an opaque enamel, it is desirable to have small particles of very high or very low refractive index uniformly dispersed throughout the enamel glass. According to the way in which the fulfillment of these conditions is attempted, an enamel may be classified into two general types, which for convenience will be designated as types I and II. Most commercial enamels are combinations of the two types.

(1) Type I Enamels

Type I enamels are made opaque by adding an opacifying material to the raw batch in sufficient quantity so that some of it will remain undissolved during the smelting operation. The opacity of enamels of this type depends largely on the solubility of the opacifying material in the enamel glass at smelting temperatures. In order to aid the dispersion of the opacifier, the raw batch should be mixed thoroughly and an enamel should be used that is highly fluid at smelting temperatures and yet will dissolve little or none of the opacifying material. The dispersion may also be improved by adding the opacifier as a compound which will decompose during smelting and leave the desired material in a finely divided form.

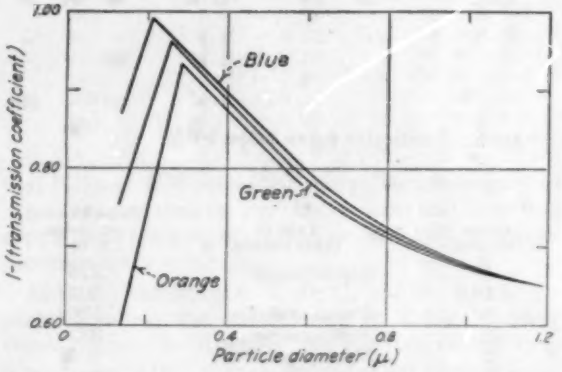


FIG. 1.—Approximate reflectance vs. particle size (data from Stutz[1]).

Enamels of this type usually tend to lose opacity during smelting and should therefore be prepared at as low a temperature as is consistent with the formation of a satisfactory glass. The two reasons for the loss in reflectance are as follows: (1) The opacifier particles tend to dissolve during smelting until the glass becomes saturated; until this state is reached, therefore, there will be a decrease in reflectance owing to a disappearance of the opacifying material. (2) Even if no solution occurs, there is usually a strong tendency toward the formation of larger individual particles with the disappearance of the smaller ones; this may be brought about by coagulation or by solution and recrystallization. The result in either case is usually to produce particles which scatter the light less effectively and thus to cause a loss in reflectance.

* Presented at the Forty-Third Annual Meeting, The American Ceramic Society, Baltimore, Md., April 1, 1941 (Enamel Division). Received April 2, 1941.

[1] G. F. A. Stutz, "Scattering Light by Dielectrics of Small Particle Size," *Jour. Franklin Inst.*, **210** [1] 67–85 (1930); *Ceram. Abs.*, **10** [4] 306 (1931).

If the reflectance of the fired enamel is plotted against the smelting temperature, a curve similar to the one in Fig. 2 will be obtained for enamels of this type. The maximum reflectance will be reached at a relatively low temperature. It will be limited by the quantity and particle size of the opacifier and by the uniformity with which it is distributed throughout the enamel. There may be a further limitation if the opacifier is added to the raw batch as a compound which must first decompose before much opacity can be developed. Once the necessary reactions have taken place the reflectance will steadily drop as the temperature is raised until at last all of the opacifier goes into solution and nothing is left but a clear glass.

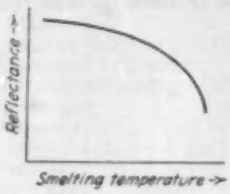


FIG. 2.

Enamels of type I usually show little change in reflectance with firing temperature.

The features of type I enamels are summarized as follows: (1) The frit is opaque even at smelting temperatures. (2) The opacifier should have low solubility in the enamel glass both at smelting and at firing temperatures. (3) The raw batch should be thoroughly mixed in order to aid in dispersing the opacifier. (4) These enamels should be smelted at the lowest temperature and shortest time that is consistent with the production of other desirable properties. (5) These enamels are relatively insensitive to smelting and firing temperature if the temperature at which the opacifier is completely soluble is not approached. (6) Provided the solubility of the opacifier is low, the less viscous the glass the better is the reflectance.

(2) Type II Enamels

The opacifier is completely dissolved during smelting in enamels of type II and then recrystallizes during the subsequent quenching and firing. The laws governing crystallization and crystal growth will first be reviewed in order to explain the action of these enamels.

Von Weimarn[2] states that the size of the particles separating during the initial stage of crystallization varies directly as the concentration of the saturated solution and inversely as the difference between the concentration of the supersaturated solution and that of a saturated solution under the same conditions. The mathematical expression is as follows:

$$G = \frac{L}{Q - L}\,(\text{constant}). \qquad (1)$$

Where G = size of particles.
Q = concentration of solution before crystallization.
L = concentration of saturated solution.

The variation in crystal size with variations in $Q - L$ for different values of L are shown in Fig. 3. Curve 1 has the lowest value of L and curve 3 the highest value.

[2] P. P. von Weimarn, "Theory of the Colloidal State of Matter," p. 27 of Colloid Chemistry, Vol. I, by Jerome Alexander. Chemical Publishing Co., New York, 1926; entire book abstracted in *Ceram. Abs.*, **5** [11] 379 (1926).

The foregoing rule applies only to the limiting condition which the solution tends to approach during the initial stage of crystallization. Studies of the devitrification in silicate systems have shown that the viscosity of the melt and the heat of formation of the crystals are also important in the development of crystals of measurable size. Typical curves, according to Tammann[3] for the rate of crystal growth, the number of crystal nuclei, and the viscosity of the melt are shown in Fig. 4. Such curves are obtained when the temperature of a single composition is varied.

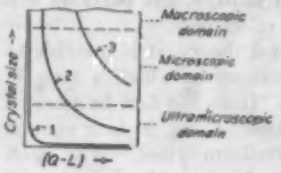


FIG. 3.—Q = concentration of solution; L = concentration of saturated solution.

The melt will be just starting to crystallize at a, which is the liquidus temperature. The number of crystal centers will be small and the rate of crystal growth will be low. As the temperature is lowered from a to b, the rate of growth will increase. The controlling factor in this range is the rate at which the heat released in the process of crystallization can be removed. On further cooling below b, the rate of growth is decreased because the increased viscosity (shown by curve 3)

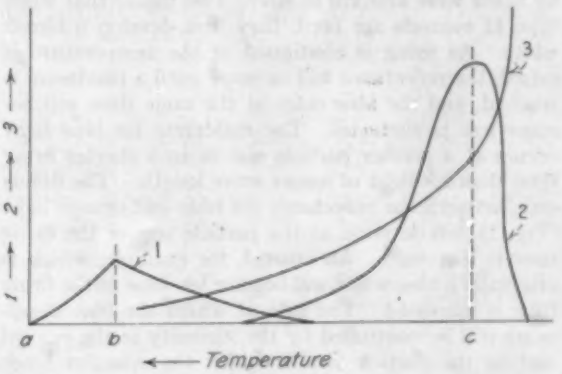


FIG. 4.—1 = rate of crystal growth; 2 = number of nuclei; 3 = viscosity.

decreases the rate at which the particles or atoms forming the crystals can migrate through the melt. Lowering the temperature also lowers the solubility, L, and increases the difference in solubility, $Q-L$ (see equation (1)). Both of these effects tend to reduce the size of the particles and to increase their number. The number of nuclei, therefore, increases until temperature c is reached. At this point, the viscosity becomes so high that it affects even the initial stage of crystallization and, on a further lowering of the temperature, the number of nuclei decreases rapidly. The temperature range from b to c is the one most favorable

[3] Gustav Tammann (translated by R. F. Mehl), The States of Aggregation. D. Van Nostrand Co., New York, 1925.

to crystal formation. Glasses heated in this temperature range will become densely opaque. The opacity will tend to drop as the limits of the range are approached. Toward the lower temperature limit (*c* or below), the glass may become blue in reflected light because of the extremely small size of the separating particles; toward the upper limit, *a*, the particles will be too large to scatter light effectively.

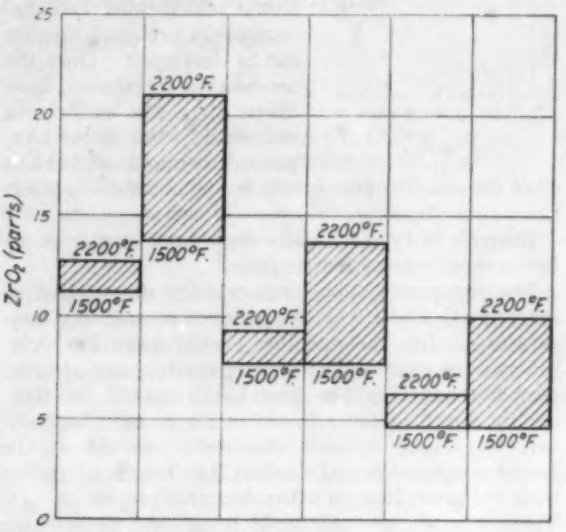
On the basis of this general theory, it is possible to tell something about the manner in which a type II enamel should be prepared. It should first be smelted above the liquidus temperature (*a*, Fig. 4) long enough to produce an optically uniform glass. The melt should then be quenched and reheated or fired at a temperature somewhere in the range from *b* to *c* (Fig. 4) and probably nearer the lower limit, *c*. If it is fired at too low a temperature, the enamels will appear blue. The opacifying particles will slowly grow in size during firing, and the reflectance of the fired enamel will show a variation similar to that illustrated in Fig. 1, except that particle size will be replaced by firing time because the separated particles will tend to grow and aggregate after they appear. The action is similar to that which occurs during the smelting of type I enamels. The change in reflectance will be less abrupt than that indicated by the curves in Fig. 1 because the fired enamels contain particles varying considerably in size, whereas the particles that were present in the suspensions used by Stutz were uniform in size. This means that when type II enamels are fired, they first develop a bluish white. As firing is continued or the temperature is raised, the reflectance will increase until a maximum is reached, and the blue color at the same time will become less pronounced. The maximum for blue light occurs at a smaller particle size or in a shorter firing time than for light of longer wave length. The difference between the reflectance for blue and orange light (Fig. 1) will decrease as the particle size or the firing time is increased. An enamel, for example, which is originally a blue-white will become less blue as the firing time is increased. The rate at which the blue disappears will be controlled by the viscosity of the enamel and by the particle size in which the opacifier tends to separate.

In the development of a satisfactory type II enamel, a large difference in the solubility of the opacifier at smelting and at firing temperatures is necessary so that a large quantity of fine particles will separate to form a highly opaque enamel. The enamel must also be fluid enough at firing temperatures so that the opacifier particles will grow sufficiently during firing to avoid a blue color.

The features of type II enamels are summarized as follows: (1) The frit is clear at smelting temperatures. (2) These enamels dissolve a large amount of opacifier at smelting temperatures and a relatively small amount at firing temperatures. (3) The raw batch should be thoroughly mixed and smelted so as to produce optical homogeneity during smelting with a minimum loss of volatile constituents. (4) These enamels are relatively sensitive to firing schedule because underfired enamels have low opacity and tend toward a blue-white.

II. Application of Theory

In order to apply this theory (which has just been discussed) to the development of enamels, something must be known of the solubility of the opacifying material in different enamel compositions at both the smelting and the firing temperatures. Such studies have been made of the solubility of zirconia in a large number of glasses.[4] Figure 5 shows the use of these data in the development of an enamel.



Glass compositions						
$Na_2O+B_2O_3+SiO_2$	100	90	90	80	80	70
CaF_2		10		10		10
Al_2O_3			10	10	10	10
ZnO					10	10

FIG. 5.—Zirconia dissolved in glasses containing 15% of Na_2O; shaded area indicates amount of zirconia dissolved at 2200°F. and crystallizing at 1500°F.

Starting at the left, the first glass contains 15% of soda and equal amounts of boric oxide and silica. This glass will dissolve a large amount of zirconia, but it shows little change in solubility from 1500° to 2200°F. Such a glass gives very low opacity even if an excess of zirconia is introduced. Owing to the high solubility of the zirconia, much of the opacifier will dissolve and the particle size of the remainder will be too large for efficient opacification. Because of the small variation in solubility with temperature, the amount of crystallization during firing will be negligible.

In the next enamel, some calcium fluoride was substituted for equal parts of boric oxide and silica. This enamel, although dissolving a large quantity of zirconia, should show an improvement in opacity because of the considerable change in solubility with temperature, and zirconia should crystallize during firing. This enamel, however, contains so much zirconia that it will be relatively viscous at firing temperatures and, therefore, the amount of crystallization may be small.

[4] B. W. King, Jr., and A. I. Andrews, "Solubility of Zirconia in Soda-Borosilicate Glasses," this issue, pp. 367–72.

This condition may be improved somewhat by the substitution of alumina for some of the boric oxide and silica, which is shown by the next two glasses in Fig. 5. The amount of dissolved zirconia has been reduced,

TABLE I

PROPERTIES OF ZIRCONIA-OPACIFIED ENAMELS

	Enamel No.										
	A	B	C	D	E	F	G	H	I	J	K
Batch compositions*											
Meltopax†	24.86	42.62	28.02	26.26	27.10						
Keystone feldspar	47.31		25.58	29.82	14.41						
Aluminum hydrate	2.55		0.44	2.37	7.28	21.53	0.67	4.53	7.31	1.61	1.61
Dehydrated borax	13.33	13.33	24.60	12.33		28.91	23.89	24.57	28.85	12.02	12.02
Zinc oxide	4.20	4.20	12.00	13.87	14.00			5.00			
Fluorspar	4.67	4.67	5.00	6.22	6.00	5.00	5.00	5.00	4.99		
Limestone	7.90	7.90			11.68	7.68	8.57	8.83	4.17	5.09	5.09
Soda niter	3.50	3.50	3.50	3.50	3.50	3.23	3.50	3.50	3.50	1.50	1.50
Soda ash	3.55	10.41	6.29						0.67		
Boric acid				9.11	19.50					3.90	3.90
Cryolite				3.96	4.00	12.00	14.75	14.00	16.00		
Quartz		23.39			9.40	28.95					
Pyrophyllite							41.13	36.02	36.19	49.50	49.50
Milled zircon							15.38	12.31	12.22	12.30	12.30
Phosphate rock					2.00						
Sodium silicofluoride										19.00	19.00
Amblygonite										2.00	
Amorox‡						9.47					
Theoretical melted composition											
Li_2O										0.14	
Na_2O	11.63	22.94	18.70	9.90	5.96	10.52	9.17	10.77	11.50	6.30	6.40
K_2O	8.58		5.13	5.49	2.86						
CaO	5.15	5.85			8.80	5.48	5.10	5.08	2.38	3.09	3.15
ZnO	4.88	5.55	14.24	16.27	16.40			5.13			
B_2O_3	10.71	12.17	20.20	16.02	12.90	20.63	17.54	17.37	20.43	12.11	12.37
Al_2O_3	11.92	0.03	6.30	8.67	9.14	14.52	11.02	11.92	13.81	14.47	14.28
SiO_2	41.71	47.31	29.50	31.70	31.39	30.75	36.23	30.25	30.38	42.10	42.80
TiO_2						0.56					
P_2O_5					0.82					1.16	
LiF										0.08	
CaF_2	5.42	6.15	5.93	7.30	7.04	5.16	5.31	5.13	5.11		
Na_3AlF_6				4.65	4.69	12.38	15.63	14.35	16.39		
Na_2SiF_6										20.55	21.00
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
ZrO_2	16.27	31.70	18.72	17.35	17.58	8.27	10.78	8.35	8.29	8.78	8.98
ZrO_2 dissolved (calculated)‖											
At 2200°F.	9.1	25.7	11.5	9.0	7.1	15.9	19.6	16.7	19.6	10.7	11.2
At 1500°F.	5.8	22.0	7.7	1.9	0.0	5.4	7.1	5.0	6.7	5.2	5.6
ZrO_2 undissolved (calculated)											
At 2200°F.	+7.2	+6.0	+7.4	+8.4	+10.5	−7.4	−8.8	−8.3	−11.3	−1.9	−2.2
At 1500°F.	+10.5	+9.7	+11.0	+15.5	+17.6	+2.9	+3.7	+3.4	+1.6	+3.6	+3.4
X-ray data (principal crystalline materials)											
Enamel frit	Monoclinic ZrO_2			Monoclinic ZrO_2 + CaF_2		CaF_2	CaF_2	CaF_2	CaF_2	CaF_2	CaF_2
Fired enamel	Monoclinic ZrO_2			Monoclinic + tetragonal ZrO_2 + CaF_2		Tetragonal ZrO_2 + CaF_2					
Type	I	I	I	I, II	I, II	II	II	II	II	II	II
Reflectance data (application weight, 64 gm./sq. ft.)											
	46.0	36.0	46.0	69.0§	63.2§	71.0§	69.0§	73.8§	70.5§	67.8§	56.8§
Temp. (°F.) for viscosity of 1.7×10^{13} poises¶											
	1050	1075	925	950	1060	975	1025	1000	950	1050	1075

* Supplied by Titanium Alloy Mfg. Co.

† Product containing oxides of sodium, zirconium, and silicon (see C. J. Kinzie, "Making Zirconia Opacifier," U. S. 1,789,316, Jan. 20, 1931; *Ceram. Abs.*, **10** [4] 257 (1931).

‡ Product essentially ZrO_2.

§ Reflectance data from Titanium Alloy Mfg. Co.

‖ Method previously described (see reference 4).

¶ Tests run on glass fibers prepared at the Titanium Alloy Mfg. Co.

there has been little or no alteration in the change in solubility with temperature, and the viscosity has probably been slightly decreased, but it is still objectionably high for satisfactory crystallization during firing.

The addition of zinc oxide to such a glass results in further improvement in its properties (shown by the two glasses at the right in Fig. 5). The amount of dissolved zirconia as well as the viscosity is reduced. The fluoride-free glass is approaching a composition which should be satisfactory for a type I enamel inasmuch as it is a relatively fluid glass and will dissolve only a small amount of zirconia.

The fluoride-bearing glass is approaching a composition which should be satisfactory as type II enamel. It is a relatively fluid glass that will dissolve a large amount of zirconia at smelting temperatures but a relatively small amount at firing temperatures. It should therefore develop considerable opacity owing to the crystallization that occurs during firing.

For type I enamels, in general, it is desirable to have a glass that will dissolve little or none of the opacifying materials during smelting. The enamels, however, must be fluid enough to permit dispersion of the opacifier during this operation and to develop satisfactory gloss when they are fired.

Type II enamels should be able to dissolve a large quantity of opacifier during smelting and to precipitate this material during firing. This change in solubility helps to produce a large quantity of opacifying material and, because $Q-L$ is large and L is small (see Fig. 3), the particles that appear will be small enough to give good opacity. The viscosity of the enamels at firing temperatures, however, must not be so high as to prevent crystallization. Such a condition would exist at temperatures below c in Fig. 4.

III. Data

A group of zirconia-opacified enamels differing widely in properties and compositions was selected for investigation, and their compositions and general properties are given in Table I.

In addition to the general information included in Table I, the results of a number of special tests are given in Figs. 6, 7, 8, and 9. Figure 6 shows the variation in reflectance with the smelting schedule for three typical type I enamels. Figure 7 illustrates the changes that take place in the opacifier when the smelting schedule is varied. The specimens for these photomicrographs were prepared by taking a sample from the molten enamel during smelting and then blowing it to form a very thin-walled bubble. All of the pieces selected for the photomicrographs had approximately the same thickness. Figure 8 shows the extreme variation in color and reflectance that was obtained with an improperly smelted type II enamel; Fig. 9 is a microphotometer curve from another sample of the same enamel.

IV. Analysis of Results

The type I zirconia-opacified enamels have the same general properties already outlined for this type. The reflectance of these enamels should vary approximately as the amount of zirconia undissolved during smelting (see Table II).

TABLE II

REFLECTANCE VS. ZIRCONIA UNDISSOLVED DURING SMELTING

	Enamel No.		
	A	B	C
Undissolved ZrO_2 at 2200°F.	7.2	6.0	7.4
Enamel reflectance smelted 1 hr. at 2200°F. and fired 3 min. at 1500°F.	46.0	36.0	46.0

The variation in the reflectance of these enamels with the smelting temperature agrees with the theoretical curve; this is shown by comparing Fig. 6 with Fig. 2. The combination type-enamels, such as D and E, are more stable during smelting.

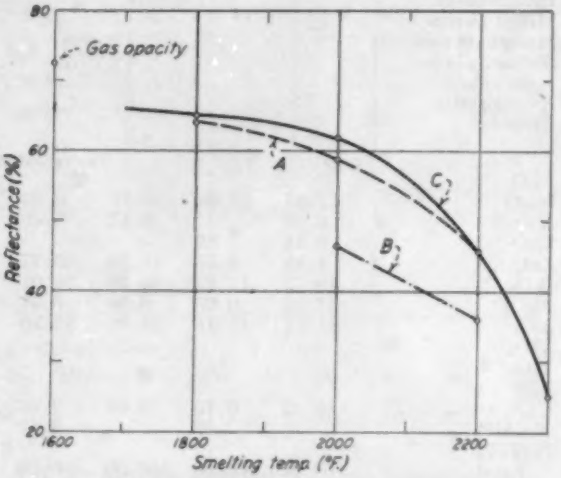


FIG. 6.—Reflectance vs. smelting temperature for zirconia enamels of type I (all enamels smelted for 1 hr. and fired 3 min. at 1500°F.); for compositions of enamels A, B, and C, see Table I.

It has been stated that a type I enamel loses opacity as the smelting temperature is increased because of the increase in the solution of the opacifier as well as in the particle size of the opacifier that remains (see Fig. 7, which shows samples of enamel C smelted at different temperatures). These pictures were taken with transmitted light at a magnification of 500 diameters; all of the sections had approximately the same thickness.

All of the type II enamels show about the same amount of zirconia available for crystallization except sample I, which had about one half as much. If the quantity of zirconia available for crystallization is the same, the reflectance should vary inversely as the viscosity (see Table III).

The only disagreement occurs possibly in enamel F, which, however, is a little low in zirconia. Part of the trouble with this enamel occurs because of the difficulty in obtaining a uniform glass during smelting. The raw batch contains a large quantity of quartz and aluminum hydrate, both of which go into solution rather

slowly. As a result, the glass in which the opacifier is dissolved is not always the glass that is indicated by the melted composition. This enamel therefore tends to develop a blue color owing to the crystallization of very small particles during firing. This color is due to fine particles as is shown by the following example.

If the opacifier crystallizes during firing, the reflectance of the fired piece should show curves similar to those in Fig. 1 in which the particle size is replaced by the firing time, as was discussed in section I (2). Such tests were run on enamel F, and the results are shown in Fig. 8. At the beginning of the test, enamel F was decidedly blue in color, and the rate of crystal growth was very slow (see Fig. 8). The curves are similar to those in Fig. 1 except that the maximum in reflectance is much less pronounced. This is to be expected when particles of a number of different sizes are present and the light source is not monochromatic.

That the blue color is due to particle size may be demonstrated in another way. The spectrophotometer curve (Fig. 9) was obtained on a sample of enamel F, which developed a pronounced blue color. If the color were due to the presence of very small particles, the scattering coefficient should vary inversely as the fourth

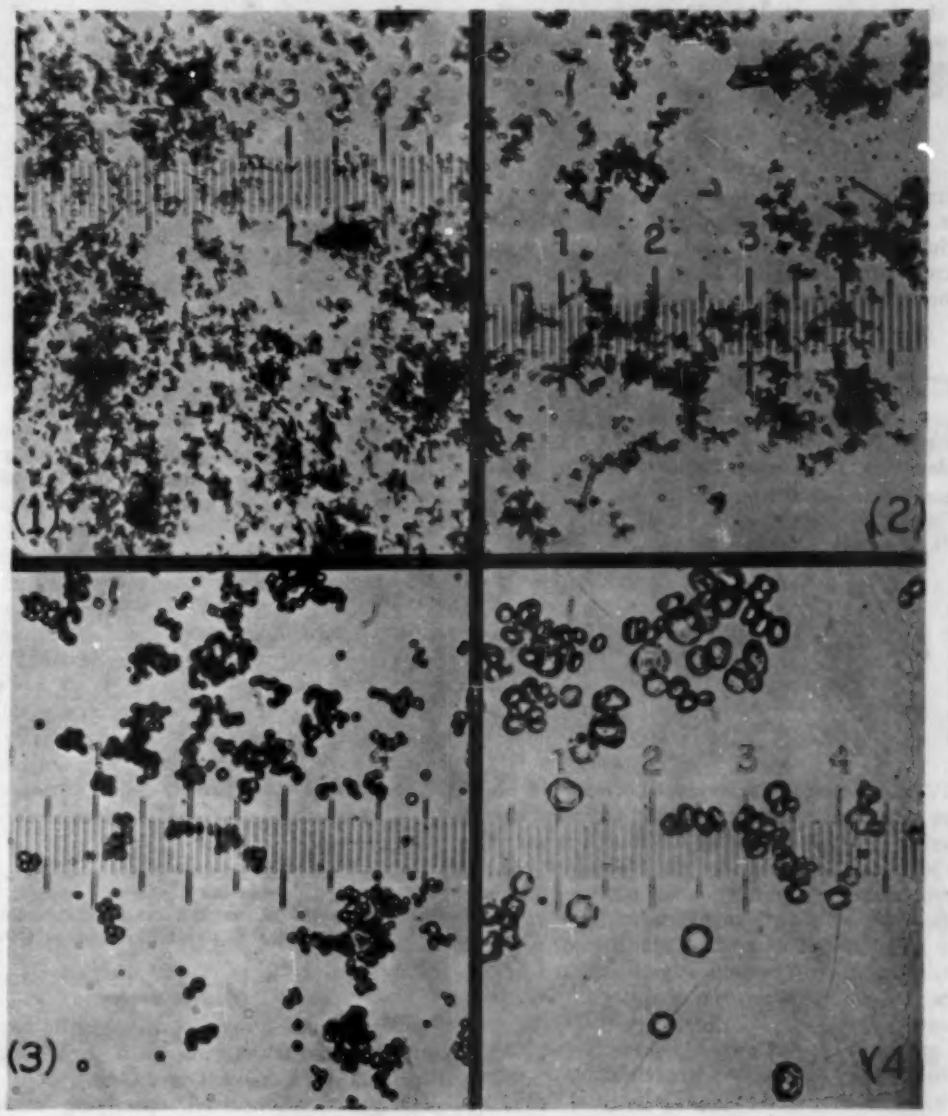


FIG. 7.—Photomicrographs of enamel C; transmitted light 5000×; all enamels smelted for 1 hr.

No.	Smelting temp. (°F.)	Reflectance (64 gm./sq. ft.)	No.	Smelting temp. (°F.)	Reflectance (64 gm./sq. in.)
1	1700	66	3	2100	55
2	1900	64	4	2300	25

TABLE III

REFLECTANCE VS. VISCOSITY AND ZIRCONIA UNDISSOLVED AT 1500°F.

Column (1) temp. (°F.) at which viscosity is 1.7×10^{13} poises; (2) reflectance (64 gm./sq. ft.); (3) ZrO_2 undissolved at 1500°F.

Enamel	(1)	(2)	(3)
I	950	70.5	1.6
I (+2% of ZrO_2)		72.5	3.6
F	975	71.0	2.9
H	1000	73.8	3.4
G	1025	69.0	3.7
J	1050	67.8	3.6
K	1075	56.8	3.4

power of the wave length (λ). The scattering coefficients, s, were calculated from the spectrophotometer curve, using the Kubelka and Munk equation,[8] and the constants for an equation of the form,

$$s = k_1 + \frac{k_2}{\lambda^4},$$

were determined for points at the ends of the curve. Values for s were then calculated and compared with the experimental data. The constant, k_1, was introduced because there appeared to be some white particles in the enamel; the results are shown in Table IV.

TABLE IV

COMPARISON OF CALCULATED AND EXPERIMENTAL VALUES FOR SCATTERING COEFFICIENT

Column (1) wave length of light (μ); (2) reflectance (%) from Fig. 9; (3) scattering coefficient (reflectivity assumed to be 100%); (4) values for scattering coefficient (s from equation, $s = 0.0078 + \frac{0.00162}{\lambda^4}$)

(1)	(2)	(3)	(4)
0.400	56.4	0.071	0.0711
0.440	48.8	0.051	0.0511
0.480	42.4	0.039	0.0384
0.520	37.0	0.031	0.0300
0.560	32.4	0.025	0.0243
0.600	28.5	0.021	0.0203
0.640	25.5	0.017	0.0175
0.680	23.0	0.015	0.0154
0.700	22.0	0.014	0.0145

Table IV shows that the agreement between the observed and calculated values is good and indicates that the scattering varies inversely as the fourth power of the wave length of the incident light. The blue color is produced, therefore, by very small particles which scatter the light of short wave length (blue) more effectively than that of long wave length (red). The blue color, therefore, can be seen, whereas the red light penetrates the enamel layer and is absorbed by the ground coat.

In the group of type II enamels studied, the large changes in zirconia solubility with temperature were due to the presence of a large fluoride content (usually around 20%).

Low zirconia solubility at firing temperatures is obtained by using low-soda, high-alumina glasses.

[8] P. Kubelka and F. Munk, "Ein Beitrag zur Optik der Farbenstriche," *Z. tech. Physik*, 12, 593 (1931).

The presence of a large fluoride content plus the necessity for obtaining a uniform glass are the chief factors in determining the smelting schedule. The following procedure in general is recommended. The batch should be heated at a moderate temperature (2000° to 2100°F.) with as little circulation of the furnace gases and as little mixing of the batch as possible. After the batch has melted down, the temperature should be dropped to just above that at which crystallization will start, probably around 1800°F. The glass should then be soaked until a high degree of uniformity is attained.

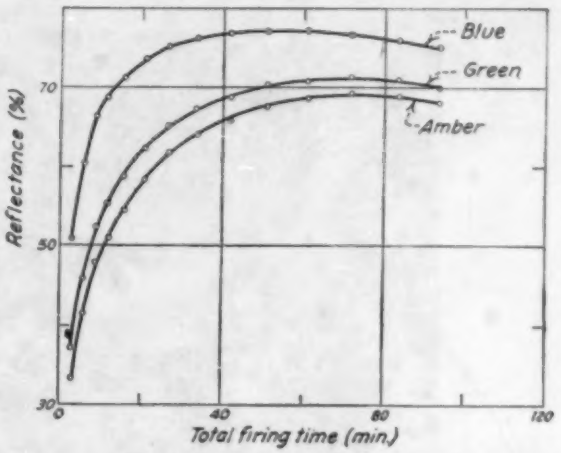


FIG. 8.—Effect of repeated firing on enamel F smelted at 1 hr. at 2200°F. and fired at 1500°F.; weight, 63.9 gm./sq. ft.

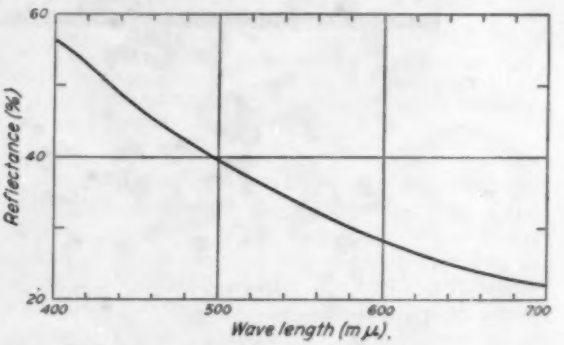


FIG. 9.—Spectrophotometer curve for enamel F smelted 1 hr. at 2000°F. and fired 3 min. at 1500°F.

V. Summary

Opaque enamels may be divided into two types according to the manner in which their opacity is produced. Type I enamels owe their opacity to a large quantity of undissolved opacifying material. The opacity of type II enamels is the result of material that dissolves during smelting and crystallizes during cooling or firing.

Type I enamels should have a low viscosity, but they should dissolve as little opacifier as possible.

Type II enamels should dissolve a large quantity of opacifying material during smelting, but at firing temperatures they should have low viscosity and low solubility so that the opacifier which has been dissolved will crystallize.

The blue color of type II enamels is often caused by the presence of very fine particles.

Acknowledgment

The authors wish to express their indebtedness to C. J. Kinzie and to the members of the Research Staff of the Titanium Alloy Manufacturing Company for their helpful suggestions throughout the course of this work. They also wish to thank B. D. Bruce, ceramic engineering student at the University of Illinois, for his assistance in preparing the enamels.

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SOLUBILITY OF ZIRCONIA IN SODA-BOROSILICATE GLASSES*

BY BURNHAM W. KING, JR., AND ANDREW I. ANDREWS

ABSTRACT

The solubility of zirconia at 1500° and at 2200°F. was determined for glasses containing Na_2O, B_2O_3, Al_2O_3, and SiO_2. The solubility at these same temperatures was also determined for glasses containing equal parts of boric oxide and silica and one or more of the following constituents in quantities of 10, 20, or 30%: Li_2O, Na_2O, K_2O, MgO, CaO, SrO, BaO, ZnO, Al_2O_3, CaF_2, and Na_3AlF_6.

I. Introduction

It was realized as early as 1911 that the effectiveness of zirconia as an opacifying material is largely dependent on its solubility in the glass in which it is used.[1] Clear glasses containing as much as 20% of zirconia[1,2] have been reported in several cases. Few systematic studies however, have been made of the solubility of zirconia in mixtures approximating the compositions of glasses or enamels. D'Ans and Löffler[3] studied part of the system Na_2O–SiO_2–ZrO_2. Kinzie and Commons[4] established some general rules concerning the effect on opacity of a number of oxides used with zirconia. Their conclusions were based mainly on results obtained with glaze compositions. Andrews and Gates[5] have recently determined the effect of variations in the composition of a typical enamel on the amount of a zirconia opacifier which it would dissolve.

The object of the present study was to make a systematic study of the solubility of zirconia in a large number of simple glasses to obtain data for estimating the solubility of zirconia in enamel compositions. It was decided to determine the amount of zirconia which the glasses will dissolve at 1500° and 2200°F. because enamels are usually fired and smelted at these respective temperatures.

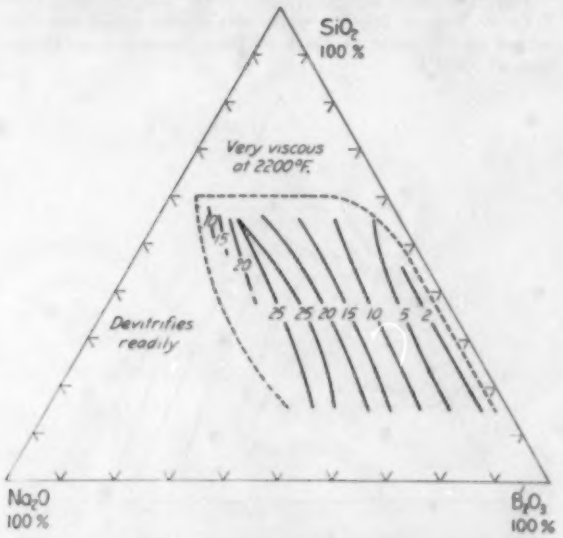

FIG. 1.—Glass compositions (% by weight), Na_2O + B_2O_3 + SiO_2 = 100%; parts of zirconia which may be added to 100 parts of glass without causing crystallization at 1500°F.

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* Presented at the Forty-Third Annual Meeting, The American Ceramic Society, Baltimore, Md., April 1, 1941 (Enamel Division). Received April 2, 1941.

[1] August Hartmann, "Zirkonemail," *Keram. Rundschau*, 19, 118 (1911).

[2] V. Dimbleby, S. English, E. M. Firth, F. W. Hodkin, and W. E. S. Turner, "Transparent Zirconia-Containing Glasses," *Jour. Soc. Glass Tech.*, **11** [41] 52–64 (1927); *Ceram. Abs.*, **6** [9] 376 (1927).

[3] J. D'Ans and J. Löffler, "System Na_2O–SiO_2–ZrO_2," *Z. anorg. allgem. Chem.*, **191** [1] 1–35 (1930); *Ceram. Abs.*, **9** [11] 985 (1930).

[4] C. J. Kinzie and C. H. Commons, "Effect of Zirconium Oxide in Glasses, Glazes, and Enamels," *Jour. Amer. Ceram. Soc.*, **17** [10] 283–87 (1934).

[5] A. I. Andrews and R. W. Gates, "Solubility of a Zirconium Oxide Opacifier in Enamel Glasses," *ibid.*, 23 [10] 288–90 (1940).

II. Procedure

The method used in this investigation was essentially one of trial and error. If the original glass was clear, zirconia was added in 2% steps until cloudiness resulted; if a glass contained undissolved zirconia, the amount of the oxide was decreased until saturation was reached; and if it was suspected that the melts were made opaque by the separation of some material other than a zirconium compound, the glasses were examined with a petrographic microscope.

The general procedure used for the solubility studies was as follows:

(1) Batches of 50 gm. each were weighed and thoroughly mixed. The materials used were chemically pure except the cryolite, borax, and zirconia (the latter contained 1% of SiO_2).

(2) These batches were smelted at 2200°F. in fireclay crucibles, and the melts were stirred occasionally to improve their uniformity. As soon as a batch melted to a clear glass, it was removed from the furnace. If a melt remained cloudy or opaque after 4 hr. at 2200°F., the zirconia content was considered to be too high and the test was repeated until a composition was reached which would melt to a clear glass. A batch that was slightly cloudy after 4 hr. at 2200°F. was believed to be saturated at that temperature.

(3) Those compositions melting to clear glasses were reheated for 24 hr. at 1500°F. and were again examined for cloudiness. A glass that was slightly cloudy was considered to be saturated with zirconia unless fluorides or immiscible liquids were present. A microscopic examination was necessary under these circumstances.

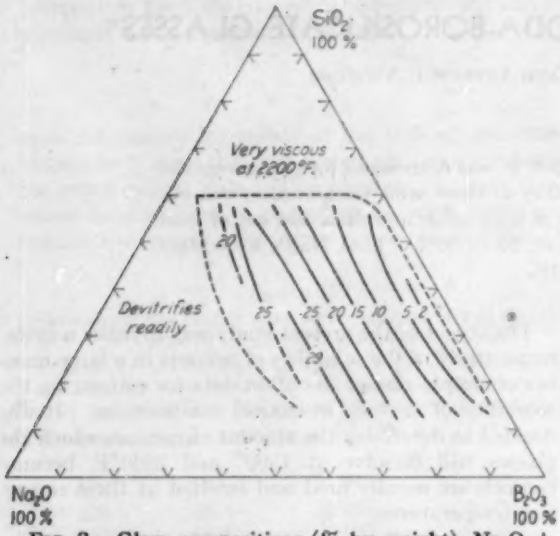

FIG. 2.—Glass compositions (% by weight), $Na_2O + B_2O_3 + SiO_2 = 100\%$; parts of zirconia which may be added to 100 parts of glass without causing crystallization at 2200°F.

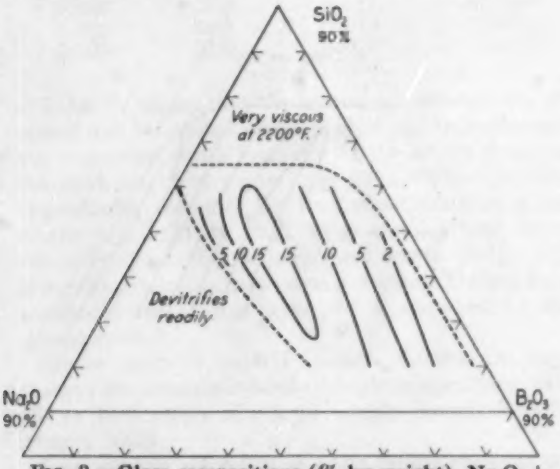

FIG. 3.—Glass compositions (% by weight), $Na_2O + B_2O_3 + SiO_2 = 90\%$ and $Al_2O_3 = 10\%$; parts of zirconia which may be added to 100 parts of glass without causing crystallization at 1500°F.

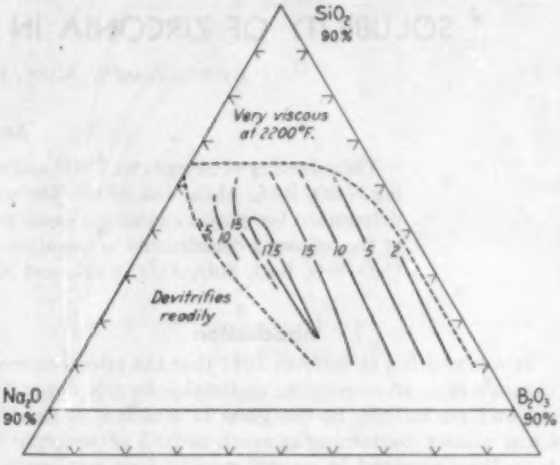

FIG. 4.—Glass compositions (% by weight), $Na_2O + B_2O_3 + SiO_2 = 90\%$ and $Al_2O_3 = 10\%$; parts of zirconia which may be added to 100 parts of glass without causing crystallization at 2200°F.

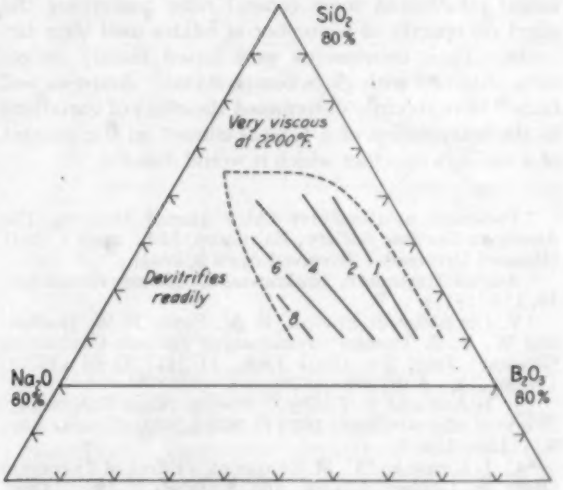

FIG. 5.—Glass compositions (% by weight), $Na_2O + B_2O_3 + SiO_2 = 80\%$ and $Al_2O_3 = 20\%$; parts of zirconia which may be added to 100 parts of glass without causing crystallization at 1500°F.

III. Data

The zirconia solubility data are summarized in Figs. 1 through 15. The amount of zirconia dissolved in the various glasses is reported as parts of zirconia per 100 parts of the other constituents on the basis of their theoretical melted composition. The base glass is always reported in percentage of composition before the zirconia is added. All of the glasses were soda-borosilicates with an oxide or fluoride usually added.

Figures 1 through 6 show the solubility of zirconia in soda-borosilicate glasses containing 0, 10, and 20% of alumina. Figure 7 is based on data taken from the foregoing diagrams and shows the effect of substituting alumina for boric oxide.

The results with soda-borosilicate glasses containing 10% of zinc oxide are given in Figs. 8 and 9.

Figure 10 shows the effect of varying the soda content and the boric oxide-silica ratios on the solubility of zirconia in glasses containing zinc oxide and alumina.

The relative effectiveness of zinc oxide and alumina in changing the zirconia solubility is illustrated in Fig. 11.

Figure 12 shows the effect of 10% of fluorspar, sodium fluoride, or cryolite, respectively, as well as the relatively large change in solubility with temperature which is brought about by a fluoride addition.

Figure 13 shows the effect of the alkalis; Fig. 14, the effect of alkaline earths.

When changes in compositions were made, it was convenient to make substitutions at the expense of boric oxide and silica although the ratio of these two materials remained constant. This was done in all cases except

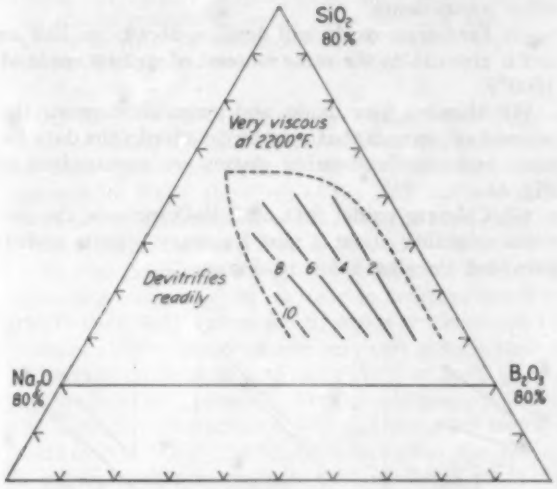

FIG. 6.—Glass compositions (% by weight), $Na_2O + B_2O_3 + SiO_2 = 80\%$ and $Al_2O_3 = 20\%$; parts of zirconia which may be added to 100 parts of glass without causing crystallization at 2200°F.

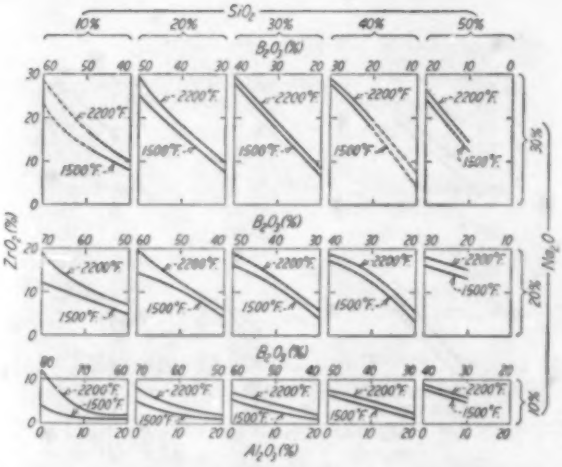

FIG. 7.—Effect of substituting Al_2O_3 for B_2O_3 on ZrO_2 solubility; zirconia dissolved per 100 parts of glass.

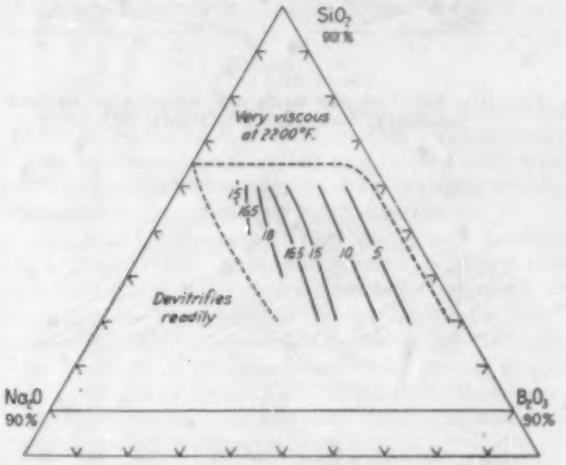

FIG. 8.—Glass compositions (% by weight), $Na_2O + B_2O_3 + SiO_2 = 90\%$ and $ZnO = 10\%$; parts of zirconia which may be added to 100 parts of glass without causing crystallization at 1500°F.

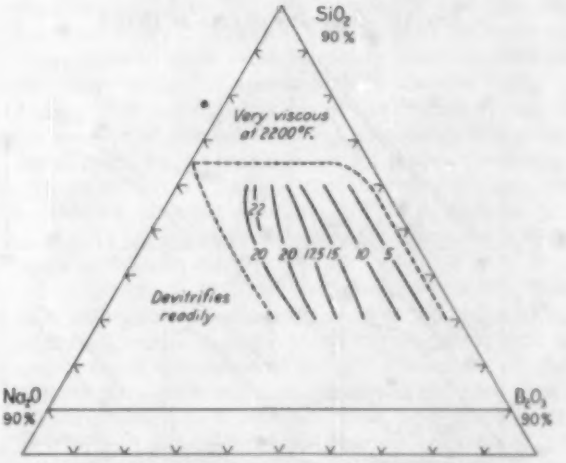

FIG. 9.—Glass compositions (% by weight), $Na_2O + B_2O_3 + SiO_2 = 90\%$ and $ZnO = 10\%$; parts of zirconia which may be added to 100 parts of glass without causing crystallization at 2200°F.

for the systems in which B_2O_3 and SiO_2 appear as components. All of the diagrams, therefore, that show the effects of the variation in zirconia solubility with soda content (such as Figs. 10, 12, 13, and 14) illustrate the results obtained when Na_2O is substituted for B_2O_3 and SiO_2 (with the ratio of B_2O_3 to SiO_2 constant) and the other constituents remain unchanged except for the zirconia.

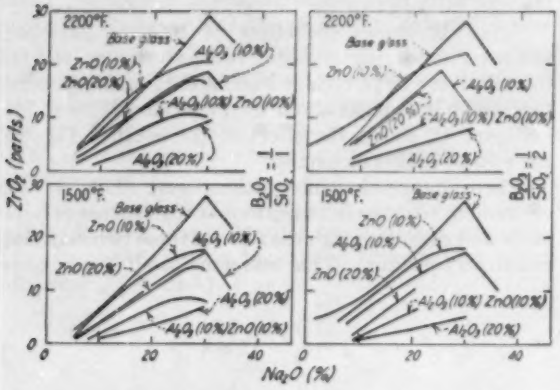

FIG. 10.—Effect of zinc oxide and alumina on zirconia solubility; base glass Na_2O–B_2O_3–SiO_2.

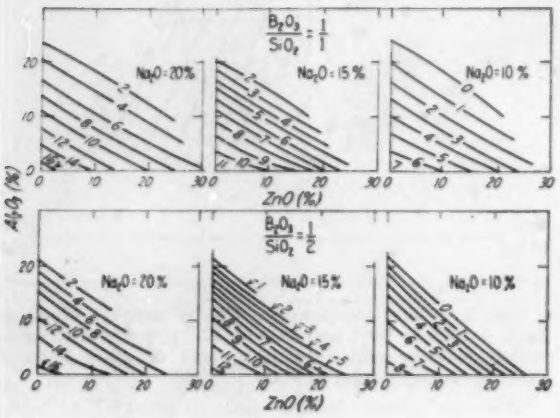

FIG. 11.—Solubility of ZrO_2 at 1500°F.

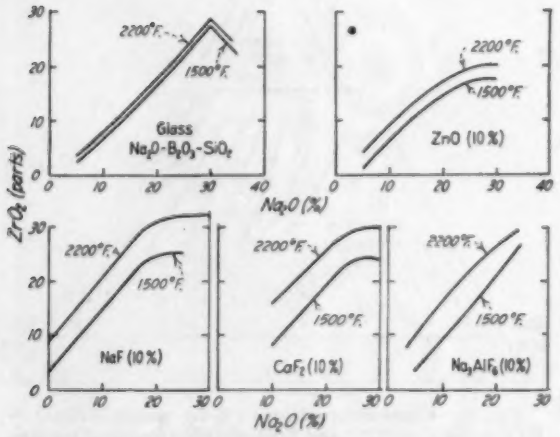

FIG. 12.—Solubility of ZrO_2 in glasses containing equal parts of B_2O_3 and SiO_2.

IV. Application of Solubility Data

The solubility of zirconia in a large number of glasses may be read directly from the foregoing data. For more complex glasses, the following rules have been found to apply with reasonable accuracy.

(1) The effects, in general, of the various oxides are approximately additive. As the addition is increased, however, those reducing the solubility are more effective and those increasing it are less effective.

(2) The amount of zirconia dissolved is proportional to the alkali content, but the rate of change of solubility with a change in alkali content is controlled by the other constituents.

(3) Potassium oxide will dissolve about one half as much zirconia as the same amount of sodium oxide at 1500°F.

(4) Alumina, zinc oxide, and magnesia decrease the amount of zirconia that may be dissolved; the data for zinc- and alumina-bearing glasses are summarized in Fig. 11.

(5) Calcium oxide, SrO, and BaO increase the zirconia solubility about 1 part for every 5 parts added, provided the glass is low in alumina.

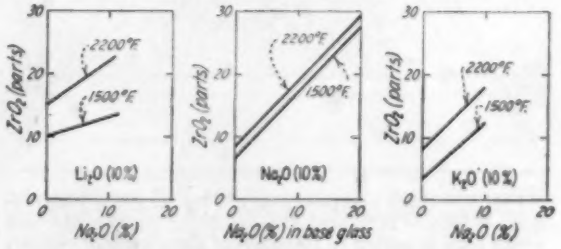

FIG. 13.—Effect of R_2O oxides on solubility of zirconia in glasses containing equal parts of B_2O_3 and SiO_2.

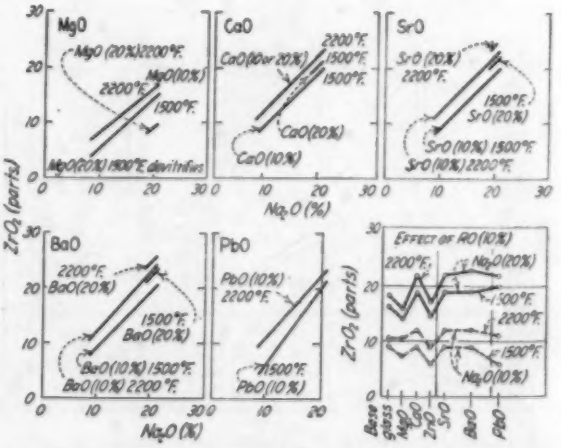

FIG. 14.—Effect of RO oxides on solubility of zirconia in glasses containing equal parts of B_2O_3 and SiO_2.

(6) Silica, boric oxide, aluminum fluoride, and calcium, strontium, or barium oxides in high-alumina melts have little or no effect on the zirconia solubility.

(7) The effect of CaF_2 or NaF at 1500°F. is the same as that of an equivalent amount of CaO or Na_2O, respectively (see Fig. 15).

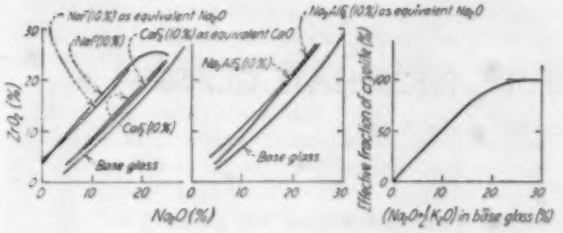

FIG. 15.—Effect of fluorides on solubility of zirconia in glasses containing equal parts of B_2O_3 and SiO_2. Curve at right shows effectiveness of equivalent Na_2O in cryolite in increasing ZrO_2 solubility.

(8) At 1500°F. and in glasses that contain 20% or more of Na_2O, the NaF in cryolite has the same effect as the equivalent amount of Na_2O. For smaller amounts of Na_2O, the effect of the NaF in the cryolite decreases as the amount of Na_2O in the base glass decreases; this effect is shown in Fig. 15.

(9) For fluoride-free glasses, the increase in zirconia solubility caused by an increase in temperature from 1500° to 2200°F. amounts to about 2 parts for 100 parts of glass except for a few very soft glasses, such as those that are high in zinc oxide (20% of ZnO) or very low in silica (15% of SiO_2). For fluoride-bearing glasses, the solubility is increased about 3 parts for every 5 parts of NaF, CaF_2, or Na_3AlF_6, provided the change in solubility is greater than that of the 2 parts per 100 minimum mentioned previously.

V. Calculations

The estimation of the solubility of zirconia in a complex glass is illustrated in the following example.

	Melted composition (%)	Melted composition omitting ZrO_2 (%)
Na_2O	8.43	9.90
K_2O	4.67	5.49
ZnO	13.87	16.27
B_2O_3	13.67	16.02
Al_2O_3	7.39	8.67
SiO_2	27.04	31.70
ZrO_2	14.79	
CaF_2	6.22	7.30
Na_3AlF_6	3.96	4.65
Total	100.00	100.00

(1) Solubility at 1500°F.

Equivalent Na_2O: Na_2O from $Na_3AlF_6 = 0.443 \times 4.65 = 2.06$.

Percentage ($Na_2O + \frac{1}{2} K_2O$) in base glass = 9.90 + 2.75 = 12.65.

Effectiveness of equivalent Na_2O from cryolite as taken from curve in Fig. 15 = 70%.

2.06 (0.70) = 1.442.

Total effective Na_2O = Na_2O + effective Na_2O from cryolite + $\frac{1}{2} K_2O$ = 9.90 + 1.44 + 2.75 = 14.09.

The zirconia solubility may be determined from Fig. 10 by using the following data and interpolating between sets of curves with varying soda content.

Na_2O	14.09
Al_2O_3	8.67
ZnO	16.27
B_2O_3:SiO_2 = 1:2 (approximately)	

Estimated zirconia solubility at 1500°F = 1.9 parts per 100 parts of other constituents.

(2) Solubility at 2200°F.

Total fluoride content = $Na_3AlF_6 + CaF_2$ = 11.95.

Increased zirconia solubility = (fluoride content) × (0.6) = 11.95 × 0.6 = 7.18.

Estimated zirconia solubility at 2200°F. = solubility at 1500°F. + increased solubility due to fluorides = 1.9 + 7.2 = 9.1 parts of zirconia per 100 parts of other constituents.

VI. Discussion

The amounts of dissolved zirconia were determined to the nearest percent in these studies. The accuracy of the data probably is not that good because some error is to be expected from solution of the crucibles or volatilization of some of the raw batch constituents.

The data for the tests at 1500°F. are more accurate than those at 2200°F. because a longer soaking period was used and the glasses were therefore more nearly at equilibrium. It is believed, however, that the information is sufficiently accurate to determine the probable amounts of zirconia dissolved in enamel glasses inasmuch as they are subjected to relatively short heat-treatments during smelting and firing and therefore only approach equilibrium condition.

Figures 1 through 9 show that the amount of zirconia dissolved in glasses containing Na_2O, Al_2O_3, B_2O_3, and SiO_2 and in those containing Na_2O, ZnO, B_2O_3, and SiO_2 depends mainly on the sodium oxide content up to about 30%. Above this soda content, the glasses tend to devitrify completely and the zirconia solubility decreases. Variations in the ratio of boric oxide to silica cause relatively small changes in solubility, except for glasses high in alumina (20% of Al_2O_3). For a constant ratio of boric oxide to silica, the amount of zirconia dissolved, in general, is directly proportional to the soda content for glasses containing up to about 30% of Na_2O. This statement is borne out by the fact that the solubility curves in Figs. 10, 12, 13, and 14 are approximately straight lines over a wide range of the soda content.

The effect of fluorides on zirconia solubility at 1500°F. in general is about the same as their equivalent oxides. Cryolite appears to be an exception, and a special curve was prepared for this component on the basis of the potash and soda content of the base glass.

Every melt which was saturated with zirconia at 2200°F. and which developed opacity on soaking at 1500°F. showed that zirconia had separated in its monoclinic form if the soda content was less than about 30%. There was a tendency for complex silicates to form in those melts containing more soda.

Acknowledgment

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PHOSPHATES IN CERAMIC WARE: IV, PHOSPHATE GLASSES*

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Abstract

Phosphorus pentoxide, which was used first to improve the color of heavy flint glasses, was later recognized as a valuable constituent of optical glasses, and the excellent ultraviolet transmission and low softening points of phosphate glasses have been found recently. Glasses that have a high content of P_2O_5 have poor chemical resistivity, but this drawback is largely overcome by the addition of alumina. A possible picture of the constitution of phosphate glasses is presented, and the effect of alumina is explained. Some of the properties of the phosphate glasses have been investigated and correlated with their chemical composition and structure.

I. Introduction

The first two papers of this series discussed phosphate opal glasses[1] and bone china,[2] two ceramic products which have been known for a long time. These studies showed that apatite crystals, which are formed in both products, cause opacity in the opal glasses and take part in forming the rigid structure of bone china.

II. Application of Phosphate Glasses

The systematic introduction of phosphates as constituents of clear glasses is relatively new. But Gillinder,[3] as early as 1854, described in detail the preparation of sodium phosphate from bone ash in a glass plant and the improvement of the color and brilliancy of the famous English flint glass by small additions of this product. This application was probably derived from the bleaching effect of phosphates in ceramic bodies.

Schott[4] and his co-workers studied a large number of glassforming oxides in their search for a new type of optical glass, and their use of phosphates extended the range of optical glasses. Because phosphate glass has a larger index of refraction than silicate glass of the same dispersion, it is better adapted for achromizing borate-flint glasses. The problem of flattening the primary and secondary image surface simultaneousyl was first solved in 1888 in an imperfect way by Miethe, who used a combination of a phosphate crown and a borate flint. His experiments showed a superiority over the best-known objectives up to that time. Because this first anastigmatic objective lacked chemical durability, the optical phosphate glasses were not only abandoned shortly after their introduction in 1902 despite their valuable properties but further research on phosphate glasses was discouraged.

The composition, refractive indices, and ν-values of two typical examples are given in Table I.

Table I

	P_2O_5	B_2O_3	K_2O	MgO	BaO	Al_2O_3	As	n_D	ν
(1)	70.5	3.0	12.0	4.0		10.0	0.51	1.5159	70.0
(2)	54.0	3.0			40.0	1.5	1.51	1.5760	65.2

(1) Light phosphate crown; (2) dense barium phosphate crown.

Interest in phosphate glasses has been revived recently because of their high transmittance for ultraviolet light. In 1894, Eder and Valenta[5] found that the phosphate crowns of Schott were superior to other optical glasses in ultraviolet transmission. The application of ultraviolet glass, however, increased rapidly when the valuable physiological properties of ultraviolet light were discovered in about 1925. Except for the very expensive silica glass, practically no glass was available which met all of the requirements.

The alkali-free borate glasses of Fritsch[6] and of

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* Presented at the Forty-Third Annual Meeting, The American Ceramic Society, Baltimore, Md., April 1, 1941 (Glass Division). Received May 1, 1941.

† Research Fellow, Monsanto Chemical Company Fellowship, Pennsylvania State College.

[1] W. A. Weyl, "Phosphates in Ceramic Ware: I, In Opal Glass," *Jour. Amer. Ceram. Soc.*, **24** [7] 221–25 (1941).

[2] W. A. Weyl, "Phosphates in Ceramic Ware: II, Role of Phosphorus in Bone China," *ibid.*, [8] 245–47.

[3] W. M. T. Gillinder, Art of Glassmaking, 2d ed. Birmingham, England, 1854.

[4] H. Hovestadt, Jena Glass and Its Scientific and Industrial Applications. Macmillan and Co., London, 1902.

[5] J. M. Eder and E. Valenta, "Absorption Spectra of Colorless and Colored Glasses," *Denkschrift der Mathem Naturw. Klasses, Akad. Wiss. Wien*, **61**, 285–95 (1894).

[6] C. Fritsch, "Ultraviolet-Transmitting Glasses," *Physik. Z.*, **8**, 518–19 (1907).

Zschimmer[7] showed devitrification and poor chemical resistivity, and Schott's Uviol glass and Chance Brothers' Vita glass, based on the absence of ferric oxide, lost their ultraviolet transmission after prolonged exposure to sunlight. Locke[8] improved the resistivity of the first group by the addition of silica.

In 1926, Hood[9] brought out a new type of ultraviolet-transmitting glass which he called Corex. It was practically a pure calcium phosphate with minor additions of boric oxide, alumina, and silica. Although the chemical resistivity of this glass was still imperfect, it was sufficient for many purposes. The I. G. Farben Company has developed improved phosphate glasses which can compete seriously with silica glass in many fields although they have a lower fusibility range. Aluminum phosphate and barium phosphate are the main constituents of this group, and glasses were made which have satisfactory chemical properties and good ultraviolet transmission as well as excellent workability that permits shaping them into tubes and into blowing burners for mercury lamps.

Grimm and Huppert[10] found that the orthophosphate of aluminum is an excellent vitrifying agent which gives phosphate glasses certain distinct properties, such as high resistivity against water and metal vapors, low coefficient of expansion, and high permeability for ultraviolet rays. Although the pure alkali borate and silicate glasses are water-soluble, the equally low-melting derivatives of aluminum phosphate were found as resistant to water as commercial glasses. The workability of these phosphate glasses was improved by the addition of B_2O_3. The same authors recently found that in replacing part of the boric oxide by zinc oxide, resistant phosphate glasses could be obtained with a softening point as low as 400°C.

Kaufmann and Bungartz[11] have pointed out that the use of barium in phosphate glasses seems to have certain advantages over calcium. Kaufmann[12] and his co-workers also found that by introducing certain activating oxides, such as tin oxide, fluorescent phosphate glasses of high efficiency could be obtained.

In addition to this more or less continuous development of phosphate glasses with the particular aim of achieving high transmission in the ultraviolet part of the spectrum, several more isolated attempts have been made to study P_2O_5 as a glassforming oxide. In 1901, Cedivoda[13] studied the sodium calcium phosphates to learn more about the application of certain "glass formulas" in relation to chemical durability. Whenever phosphate glasses had been leached out with water, acid solution resulted, whereas ordinary glasses would give off alkali chiefly. This difference in the behavior toward chemical attack had been noticed by Kohlrausch,[14] who studied a series of optical glasses, and among these, the phosphate crowns of Schott. Fritz[15] approached the same problem in glazes from a more practical viewpoint. The glaze composition represented by the Seger formula was varied by combining formulas I, II, and III with a series of acidic constituents, consisting of Al_2O_3 and P_2O_5 (series Nos. 1 to 7). Again glazes rich in PbO did not develop the typical yellowish shade in the presence of phosphates. Certain water-soluble glazes, however, became chemically resistant when fired to the body, which doubtless is the result of the combination of the phosphate glass with the alumina of the body.

	Formula No.					
	I	II	III	Series No.	P_2O_5	Al_2O_3
K_2O	0.1	0.3	0.2			
				1	1	
Na_2O	0.1	0.4	0.2	2	1	0.1
				3	2	
PbO	0.8	0.2	0.4	4	2	0.2
				5	3	
CaO		0.1	0.2	6	3	0.3
				7	3	0.15
	1.0	1.0	1.0			

In 1924, Buck[16] described the use of phosphate glasses for bottles, dishes, and stirring rods, which he found resistant to hydrofluoric acid. The metaphosphates of the alkaline earths were the chief constituents to which some aluminum metaphosphate was added. Two examples are given as follows:

No.	P_2O_5	CaO	Al_2O_3
1	77.46	10.18	12.36
2	73.15	23.77	3.08

Some interesting observations have been made recently by Stanworth and Turner[17] on the possibilities of preparing glasses containing P_2O_5, Al_2O_3, B_2O_3, and SiO_2.

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[7] E. Zschimmer, "Experiments on Relation of Ultraviolet Transmission of Glasses to Their Chemical Composition," *Physik. Z.*, **8**, 611–12 (1907).

[8] F. M. Locke, "New Glass Transmits Ultraviolet Rays," *Glass Ind.*, **7** [6] 136 (1926); *Ceram. Abs.*, **5** [8] 245 (1926).

[9] H. P. Hood, "New Ultraviolet-Transmitting Glass," *Glass Ind.*, **7** [12] 287–88 (1926); *Ceram. Abs.*, **6** [2] 55 (1927).

[10] (*a*) H. G. Grimm and Paul Huppert, "Vitreous Composition," U. S. Pat. 1,964,629, June 26, 1934; *Ceram. Abs.*, **13** [9] 236 (1934); (*b*) "Vitreous Compositions of Glasses," U. S. Pat. 2,100,391, November 30, 1937; *Ceram. Abs.*, **17** [2] 68 (1938); (*c*) "Phosphate Glass," U. S. Pat. 2,227,082, December 31, 1940; *Ceram. Abs.*, **20** [3] 69 (1941); also abstracted in *Glass Ind.*, **22** [2] 72 (1941).

[11] Waldemar Kaufmann and Everhard Bungartz, "Glass Permeable to Ultraviolet Rays," U. S. Pat. 2,031,958, February 25, 1936; *Ceram. Abs.*, **15** [5] 149 (1936).

[12] Waldemar Kaufmann, L. Eckstein, and K. Rosenberger, "Photoluminescence of Phosphate Glasses Containing Tin," U. S. Pat. 2,042,425, May 26, 1938.

[13] Franz Cedivoda, "Phosphate Glasses," *Chem. Z.*, **5**, 347–50 (1901).

[14] F. Kohlrausch, "Solubility of Some Glasses in Cold Water," *Ann. Physik*, **44**, 577–622 (1891).

[15] Helene Fritz, "Phosphate Glasses and Glazes," *Keram. Rundschau*, **26**, 195–96, 201–202, 205–206 (1918).

[16] E. C. Buck, "Fluorine-Resistant Glasses," U. S. Pat. 1,570,202, January 19, 1926.

[17] J. E. Stanworth and W. E. S. Turner, "Possibility of Preparing Glasses Containing P_2O_5, Al_2O_3, B_2O_3, and SiO_2," *Jour. Soc. Glass Tech.*, **21** [87] 368–82 (1937); *Ceram. Abs.*, **17** [9] 304 (1938).

III. Constitution of Phosphate Glasses

From the discussion of these applications, a fundamental difference between phosphate and silicate glasses appears evident. The phosphate glasses must possess properties which cannot be obtained within the field of silicate glasses. Because Warren[18] and his associates presented an independent picture of the constitution of glasses, which is not based on mere comparison with similar systems, not only the role of silicon, boron, and phosphorus but also that of constituents like alumina, which are present in quantities too small to show diffraction patterns with X rays, can be discussed.

Phosphorus pentoxide, P_2O_5, is a typical glass former. It represents the rare case wherein the vapor pressure of the glass is lower than that of a crystal having the same chemical composition. Crystalline P_2O_5 is very reactive chemically and less stable than the corresponding glassy phase because different polymers are involved and chemical reactivity and solubility decrease with polymerization. The tendency of the P_2O_5 to polymerize is noticeable even in the acidic phosphates. Hautefeuille and Perrey[19] found that the vapor pressure of P_2O_5 decreases rapidly above 250°C. due to polymerization.

The fundamental difference between SiO_2 and P_2O_5 as glass formers is based on the cation-oxygen ratio. In the pure silica glass, the number of cations (silicon) is half the number of oxygen ions; the ratio is 1 to 2. Each oxygen necessarily belongs to two silicons; in other words, the tetrahedra have to share corners. Thus the ratio (1 silicon to 2 oxygen) leads to a very rigid structure. This type of binding causes the stability of the silica glass and its high melting temperature. In the same way, phosphate glasses consist of a network of tetrahedra which are linked together. Phosphorus, however, is pentavalent; the oxygen ratio of the oxide therefore is 1 to 2.5 and that provides some "single-bonded" oxygen, which is not tied up with two different phosphorus ions. Such an atomic arrangement is naturally more flexible so that the softening point is lowered. As far as the network is concerned, the structure of P_2O_5 resembles more that of sodium disilicate, $Na_2Si_2O_5$, where the cation-oxygen ratio is also 1 to 2.5. The chief difference between the two types of glass is that the silicate has to contain a certain amount of alkali to balance the charges of those oxygens, which exceed the ratio 1 to 2. In the case of P_2O_5 glass, the pentavalent cation (phosphorus) is able to balance these charges. From these theoretical considerations one can conclude that the two glasses, P_2O_5 and $Na_2Si_2O_5$, resemble each other in those properties which depend on the network proper. As far as the properties that depend on the "network modifiers" are concerned, P_2O_5 glass may be expected to resemble the pure silica.

The term, "network modifiers," has been used by Warren to designate such cations as Na^+, K^+, or Ca^{++}, which do not take active part in forming the network of the glass but merely fill holes in the open structure.

It can indeed be proved experimentally that thermal expansion, softening point, and chemical resistance, properties depending to a great extent on the network, are similar in P_2O_5 and $Na_2Si_2O_5$ glasses. With respect to electrical properties and ultraviolet absorption, however, which are mainly influenced by the "network modifiers," P_2O_5 glass resembles SiO_2 glass.

Because such network modifiers as Na^+ and Ca^{++} do not enter the glass structure proper, the addition of the respective oxides, Na_2O and CaO, and others, contributes to an increase of the oxygen in the network.

If more oxygen enters the network, fewer corners are shared. The oxygen tetrahedra (which in a pure silica glass share all corners) share only three corners in P_2O_5 glass and in a sodium disilicate ($Na_2Si_2O_5$) glass and in each of these glasses will share still fewer corners with increasing additions of alkali. Figure 1 illustrates the relation of the phosphorus-oxygen and of the silicon-oxygen ratio to the corners shared. When the phosphorus-oxygen ratio of 1 to 4 is reached, no corners are shared, and a fluid melt is obtained which does not form a glass on cooling; no glasses are known of the orthosilicate and orthophosphate of sodium.

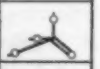
	Silicate Glasses	Phosphate Glasses	
1:2	SiO_2	$Al_2O_3 . P_2O_5$ Aluminum Orthophosphate	
1:2.25		$Al_2O_3 . 3P_2O_5$ Aluminum Metaphosphate	
1:2.3	$Na_2O . CaO . 6SiO_2$		
1:2.5	$Na_2O . 2SiO_2$ Sodium Disilicate	P_2O_5	
1:3	$Na_2O . SiO_2$ Sodium Metasilicate	$Na_2O . P_2O_5$ Sodium Metaphosphate	

FIG. 1.—Cation-oxygen ratio of silicate and phosphate glasses.

The chemical resistivity of sodium disilicate glass as well as that of pure P_2O_5 glass is extremely poor. Both substances are hygroscopic and soluble in water. To improve this property, an oxide must be added which causes the cation-oxygen ratio of 1 to 2.5 to approach that of pure silica, a ratio of 1 to 2; B_2O_3 and Al_2O_3 are oxides which act in this direction as their own cation-oxygen ratio is only 1 to 1.5. Despite the fact that boric oxide is easily soluble, it improves chemical resistivity considerably when it is added to a sodium silicate glass, and its influence on phosphoric oxide is just as striking. The compound, $B_2O_3 \cdot P_2O_5$ or BPO_4, is not only insoluble in boiling water but it is attacked by alkali only at elevated temperatures.

[18] (*a*) B. E. Warren, "X-Ray Diffraction Study of Structure of Glass," *Chem. Revs.*, **26** [2] 237–55 (1940); *Ceram. Abs.*, **19**[8] 187 (1940).

(*b*) J. Biscoe, A. G. Pincus, C. S. Smith, Jr., and B. E. Warren, "X-Ray Study of Lime Phosphate and Lime Borate Glass," *Jour. Amer. Ceram. Soc.*, **24** [4] 116–19 (1941).

[19] P. Hautefeuille and L. Perrey, "Anhydrous Phosphoric Acid," *Compt. Rend.*, **99**, 33–35 (1884).

Another way to improve the resistivity of P_2O_5 is to add alumina. This oxide may be added even to the aluminum orthophosphate composition which possesses the same cation-oxygen ratio as pure silica. This compound, $Al_2O_3 \cdot P_2O_5$, in the glassy state has exactly the same structure as a silica glass except that the centers of the tetrahedra are not formed by silicon ions but, alternately, by aluminum ions and phosphorus ions.

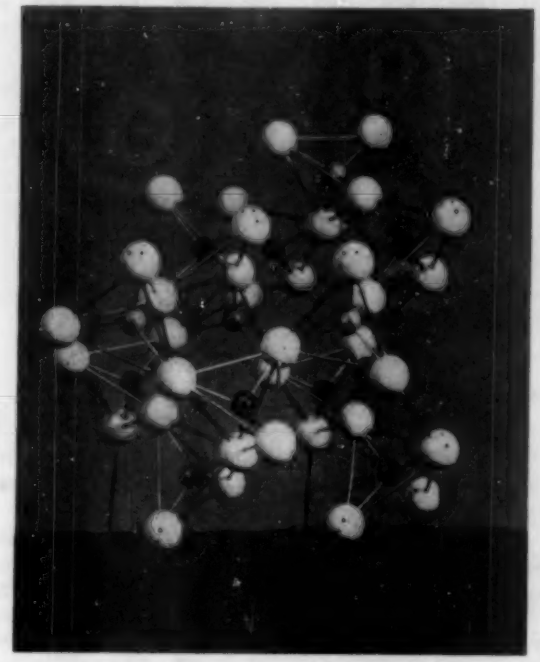


FIG. 2.—Model of aluminum orthosilicate.

Because the Al^{3+} is slightly larger and the P^{5+} is somewhat smaller than the Si^{4+}, the similarity between the two compounds is not limited to the glassy state but is evident in the crystalline compounds. Huettenlocher,[20] who determined the atomic structure of aluminum orthophosphate (Fig. 2) by means of X rays, emphasized the close similarity of its structure to that of quartz and aluminum orthoarsenate. Machatschki,[21] who had revealed the structure of the latter, even used the term, "polyquartz," for the dimensions of the unit cell are identical with that of quartz in two directions. In the direction of the *c*-axis, the length is twice that of quartz so that the unit cell can accommodate the aluminum ion as well as the phosphorus ion. (The chemical term, anhydride of a heteropoly acid, should be used here rather than the chemical term, aluminum salt of the phosphoric acid.) The glasses derived from this compound are aluminophosphates in the true sense of the word.

[20] H. F. Huettenlocher, "Structure of Aluminum Orthophosphate and of Low Quartz," *Z. Krist.*, **90**, 508–16 (1935).

[21] F. Machatschki, "Crystal Structure of Low Quartz, SiO_2, and Aluminum Orthoarsenate, $AlAsO_4$," *ibid.*, **94** [2-3] 222–30 (1936); *Ceram. Abs.*, **16** [1] 43 (1937).

The aluminum orthophosphate, like quartz, has a high melting point. It is unnecessary in these studies to replace the structure of the sodium disilicate or of the P_2O_5 by one that resembles pure silica glass. Even the metaphosphate of aluminum, the compound $Al_2O_3 \cdot 3P_2O_5$, is of considerable chemical resistivity. In the present work, therefore, this compound has been used as the basis for phosphate glasses.

IV. Scope of the Research

The first scouting experiments showed that the field of phosphate glasses is even more extended than that of silicates. It was necessary, therefore, to introduce certain limiting factors which would narrow the field and allow concentration in those areas where particularly interesting properties could be expected. The scope of this work will be extended, however, and new composition ranges will be studied.

The first limitation was the melting temperature, and all glasses were excluded which could not be melted readily at about 1400°C. This eliminated the pure aluminum phosphates which require high temperatures. The field of glass formation was further limited by the tendency to devitrify, and those areas in which glasses could be obtained only under special precautions and in little droplets were also avoided. An arbitrary limit was thus raised, which may be adjusted later to the purpose of the glass and the type of shaping used. As far as devitrification is concerned, little attention was given to the finer differences inasmuch as a glass of simple composition is more likely to devitrify than the more complex glasses. With proper combination of a greater number of constituents, it is not difficult to decrease this tendency.

A low alkali content was used in these studies in order to obtain glass of good electrical and chemical properties. Phosphate glasses, high in alkalis, approach the alkali silicates in their properties, and the primary interest of the writers was to obtain glasses as different as possible.

(1) Fields of Glass Formation

Phosphorus pentoxide itself forms a glass. Commercial P_2O_5 in its crystalline form is a strongly hygroscopic material, but when it is not properly quenched the vapor condenses and forms partly a glassy phase. Such a product is not as good a drying agent as fully crystalline material. Smits and Rutgers[22] determined the vapor pressure of phosphorus pentoxide and found that at 400°C. the pressure of the metastable crystalline material was about four atmospheres, but this dropped almost to zero when the stable glassy modification was formed.

At a higher temperature, this polymerized glassy modification decomposes again to form P_2O_5 vapor, which can be condensed either into a crystal or a glass according to cooling conditions. Campbell and Camp-

[22] A. Smits and A. J. Rutgers, "Behavior of Phosphorus Pentoxide," *Jour. Chem. Soc.* [London], **75**, 2573–79 (1924).

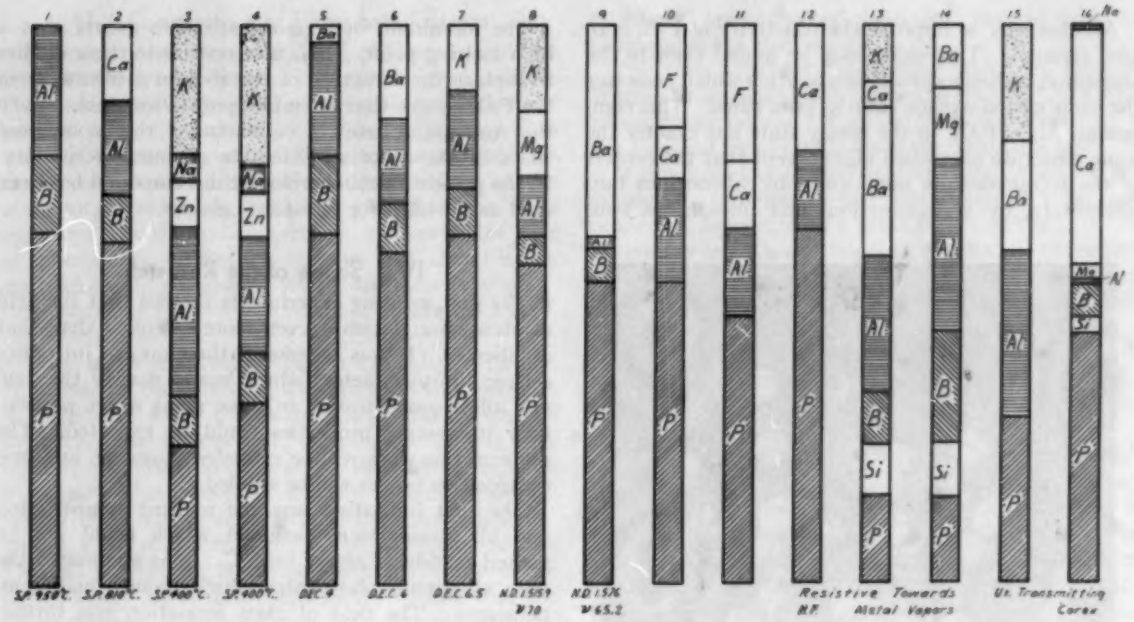


FIG. 3.—Typical composition of some phosphate glasses.

bell,[23] who studied the different modifications of P_2O_5 by means of density measurements, rates of solution, and solubilities in chloroform, concluded that the only homogeneous and the most stable form of P_2O_5 is the vitreous form because it has the lowest solubility and the highest density.

Pure P_2O_5 glass has no commercial value because it is water soluble and volatile.

P_2O_5 was introduced into the experimental melts in the form of the metaphosphates. Wherever excess of P_2O_5 over the metaphosphate is desirable, the free oxide as well as the ammonium phosphate may be used. This oxide, however, is hygroscopic, whereas ammonium phosphates give rise to ammonia fumes which are not only troublesome but may have a reducing influence on certain glassforming oxides. The use of tetraphosphoric acid was preferred in this study. It is a viscous liquid, readily flowing at about 50°C., and it contains 84% of P_2O_5 and mixes well with other ingredients.

Sodium metaphosphate is well known as a glass-forming agent from the bead test in analytical chemistry. On heating, microcosmic salt, $NaNH_4HPO_4$, decomposes with the evolution of water and ammonia and forms a sodium metaphosphate glass which has the property of adding oxides and sulfides. These compounds are dissolved, and a homogeneous glass is formed wherein the characteristic colors of the ions introduced serve to identify them.

The addition of oxides leads to pyrophosphates according to equation (1).

$$2NaPO_3 + CuO = Na_2O \cdot CuO \cdot P_2O_5. \qquad (1)$$

Cohn[24] did not detect any orthophosphate by its characteristic yellow silver salt except when devitrification occurs and no clear glass can be obtained.

Zintl and Bertram[25] found recently that sodium metaphosphate reacts with sodium sulfide forming sodium thioorthophosphate, $NaPO_3 + Na_2S = Na_3SPO_3$.

The important role of this reaction for the wetting and adherence of phosphate enamels on steel will be discussed in a later publication. The property of adding other molecules is characteristic of phosphate glasses and may be used to advantage for the incorporation of fluorine in a glass wherein opacification is undesirable. These glasses form an important basis for developing optical and ultraviolet-transmitting glasses.

The metaphosphates of calcium, barium, magnesium, zinc, and iron can be melted easily and, on cooling, they form glasses.

Aluminum metaphosphate ($Al_2O_3 \cdot 3P_2O_5$) was the chief ingredient of the glasses used in this study, although its high melting point did not give pure aluminum metaphosphate glasses within the arbitrary temperature limits. Small amounts of fluxes, however, were sufficient to produce glasses high in aluminum metaphosphate.

The metaphosphates of sodium, potassium, calcium, barium, zinc, and magnesium were investigated for use as fluxes, and it was possible to flux the aluminum metaphosphate with such basic oxides as calcium oxide,

[23] A. N. Campbell and A. J. R. Campbell, "Allotropy of Phosphorus Pentoxide," *Trans. Faraday Soc.*, **31**, 1567–74 (1935).

[24] T. H. Cohn, "Cause of Color Produced in Glasses of Anhydrous Borax and Sodium Metaphosphate by Fusion with Metallic Oxides," *Chem. News*, **129**, 32–35 (1924); *Ceram. Abs.*, **3** [10] 282 (1924).

[25] (*a*) E. Zintl and A. Bertram, "Sodium Monothioorthophosphate," *Z. anorg. allgem. Chem.*, **245**, 16–19 (1940); (*b*) "Do Water-Free Sodium Silicophosphates Exist?" *ibid.*, pp. 11–15.

TABLE II

Glass No.	Properties	Reference*	P_2O_5	SiO_2	B_2O_3	Al_2O_3	MgO	ZnO	BaO	CaO	Na_2O	K_2O	F
1	Softening point over 950°C.; fusing temp., 1450°C.	Exptl.	64.2		14.0	21.8							
2	Softening point 810°C.; fusing temp., 1450°C.	"	62.6		8.4	17.1				11.9			
3	Softening point lower than 400°C.	Ref.[19]	25.5		9.0	30.5		8.0			5.0	23.0	
4	" " " " "	"	33.0		9.0	21.0		8.0			5.0	24.0	
5	Dielectric constant, 4–5	Exptl.	63.8		14.0	21.3			0.9				
6	" " 6	"	60.1		9.3	15.0			15.6				
7	" " 6.5	"	63.1		8.8	17.7						10.4	
8	n_D = 1.5159; value = 70.0; light phosphate crown of low resistivity	Ref.[4]	57.4		5.0	11.3	11.5					14.8	
9	n_D = 1.5760; value = 65.2; dense barium phosphate crown of low resistivity	"	54.4		6.1	2.1			37.4				
10	Fluxed with CaF_2; no opacification	Exptl.	54.8			18.6				8.9			17.7
11	" " " " "	"	47.9			16.2				12.0			23.9
12	High resistivity toward HF	Ref.[18]	64.3			14.3				21.4			
13	High resistivity toward metal vapors; ultraviolet-transmitting	Ref.[19]	16.0	9.0	9.7	24.6			27.2	4.5		9.0	
14	" " " " "	"	15.7	10.0	20.0	31.3	13.0		10.0				
15	High ultraviolet transmission	"	30.0			30.0			20.0			20.0	
16	Corex, high ultraviolet transmission; low resistivity	Ref.[24]	45.2	3.2	6.2	0.5	1.1			43.0	0.8		

* Exptl. = experimental. Ref. = footnote references in text.

barium oxide, and magnesium oxide, thus approaching the ratio of an orthophosphate. Calcium fluoride proved to be not only a powerful flux but it could be introduced in quantities up to about 20% without causing opacification.

Of the acidic oxides, not only B_2O_3 but even SiO_2 could be used as fluxes.

The range of meltable glasses with a high content of alumina and P_2O_5 is small in the ternary system Al_2O_3–P_2O_5–B_2O_3, and it is not surprising that Stanworth and Turner[17] could find no vitrifiable mixtures in their scouting experiments. A small range of glass formation was found by the present writers when increasing amounts of B_2O_3 were added to aluminum metaphosphate. The addition of 8 to 12% of B_2O_3 proved to be satisfactory. Mixtures with a lower or higher B_2O_3 content were unmeltable within the present arbitrary limits. One glass within this range has been prepared by Patashinsky,[26] who found the electrical breakdown strength to be very high.

V. Characteristic Properties of Phosphate Glasses

Table II and Fig. 3 show the molecular composition of sixteen phosphate glasses containing alumina. Part of these glasses are experimental types and part are from the footnote references.

The characteristic properties are indicated. Glasses Nos. 1 and 2 have a high softening point (as determined by the method of Littleton),[27] but they were meltable within the arbitrary limits of this study. They are characterized by the complete absence of alkali. The gradual softening of an alkali-lime-silica glass is due to the fact that its bonds are of widely varying strength. A glass that contains only bonds, the strength of which is of the same order of magnitude as aluminum phosphate glass or silicate glasses high in alumina and low in alkali, shows rigidity up to high temperatures until a complete breakdown and fluidity occur. The alkali-oxygen bond is much weaker than the bonds of the Si-O, P-O, and Al-O types.

If alkali is introduced into phosphate glasses of this type, the softening point is lowered considerably, and by using both alkali and zinc oxide, glasses Nos. 3 and 4, which have a softening point below 400°C., may be obtained. These glasses possess good chemical resistivity. Normal soda-lime-silicate glasses have a softening point of between 650° and 700°C. The absence of alkali and good meltability are the essential features of the group of glasses to be used in the electrical industry.

Glass No. 5 shows that dielectric constants of 4 to 5 could be reached without sacrificing meltability. Only pure silica glass has a dielectric constant of 3.75, whereas those of normal glasses lie between 6 and 7. Introducing more alkaline earths (glass No. 6) or alkali (glass No. 7) immediately raises the dielectric constant value.

Glasses Nos. 8 and 9 represent the typical phosphate crowns discussed in the introduction. When their composition is expressed on a molecular basis, it can be seen why their chemical resistivity could not meet the requirements. The alumina content of 11.3 and 2.1% is too low to stabilize the 50 to 60% of P_2O_5.

Glasses Nos. 10 and 11 show that 24 mol. % of fluorine may be introduced into aluminum metaphosphate glass without the occurrence of opacification. The molecular compositions of glasses Nos. 12 through 16, discussed in the introduction, are listed.

[26] A. M. Patashinsky, "Breakdown Voltage of Phosphate Glass." Bachelor's thesis, Massachusetts Institute of Technology, 1939. Harvard College Library.

[27] J. T. Littleton, Jr., "Method for Measuring Softening Temperature of Glasses," *Jour. Amer. Ceram. Soc.*, 10 [4] 259–63 (1927).

Acknowledgment

The authors are indebted to the American Optical Company of Southbridge, Mass., for making available unpublished information of their own research laboratories and to J. M. Humphreys, of Rutgers University, who carried out some measurements of the dielectric constant of the phosphate glasses.

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CHARACTERISTIC INTERFERENCE PATTERNS OF PLATE AND WINDOW GLASS*

BY F. W. ADAMS AND P. W. FRENCH

ABSTRACT

An optical setup for photographing the interference patterns of a piece of flat glass is described, and photographs of characteristic patterns for several samples of plate and window glass are reproduced. Such photographs identify an unknown piece of glass as plate glass or window glass and also reveal information as to its flatness and optical polish.

I. Introduction

In order to define the flatness of a piece of glass or to identify a sample of unknown origin, a considerable amount of patience and skill have been required to place the glass of unknown origin in contact with an optical flat to obtain a positive result. A simple instrument to accomplish these results has been devised and is being used successfully. Plate glass may be distinguished easily from window glass, even on very small samples, and the flatness and perfection of the optical polish may be defined quickly by the use of this instrument.

II. Use and Description of Instrument

The instrument depends on the parallel alignment of the specimen and an optical flat under conditions of monochromatic illumination. The surface flatness is obtained readily by observing the arrangement and frequency of fringes in the resulting Newton's rings. Sufficient intensity of illumination is provided to secure a permanent photographic record of the surface with a small camera.

The setup for photographing the interference patterns is shown in Fig. 1. The light source is a sodium vapor lamp which produces nearly monochromatic light with a wave length of 6000 Å. or 0.000024 in. The light is diffused by a screen of paper or tracing cloth to provide a light source of large area. The sample is placed beneath the screen and about 24 in. from it. The optical flat, a 2-in. disk of glass $^1/_2$ in. thick, is held in a brass ring and is supported on the ends of three springs. The springs may be adjusted by leveling screws in order to place the optical flat in position with respect to the sample. The optical flat is adjusted by means of the screws until at least one point is on the field at which the distance between the optically flat surface and the sample surface is a maximum or a minimum. This point may be the center of a concentric system of bands or it may appear as a point surrounded by bands that are more or less parabolic. Usually only one type of band system appears on a surface of plate glass; on the more wavy window glass, several centers may appear although both types of curvature of the bands may be present. The interference patterns are photo-

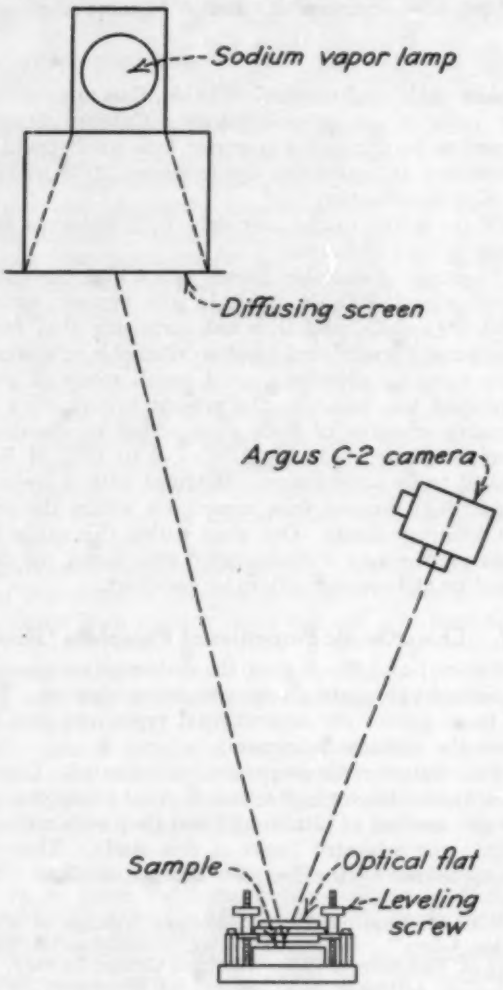

FIG. 1.—Setup for photographing interference patterns.

* Presented at the Forty-Third Annual Meeting, The American Ceramic Society, Baltimore, Md., April 2, 1941 (Glass Division). Received April 3, 1941.

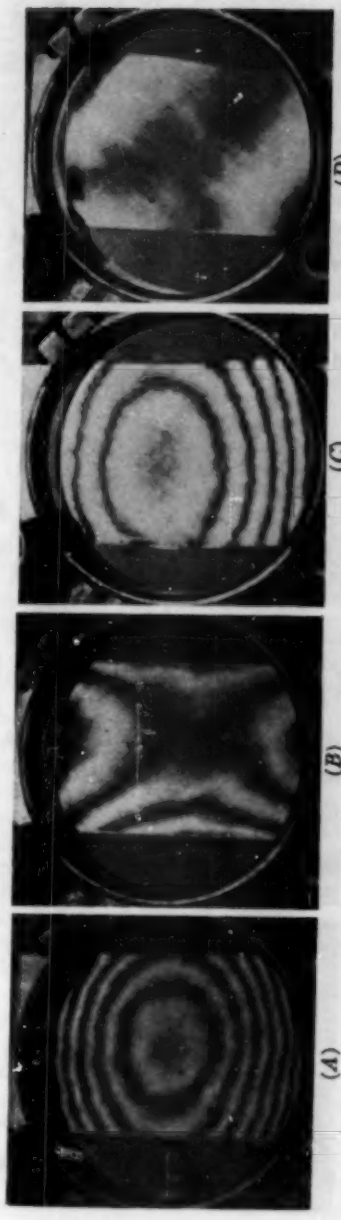

FIG. 2.—Interference patterns on plate glass: (*A*) A; (*B*) B; (*C*) Ar; and (*D*) Br.

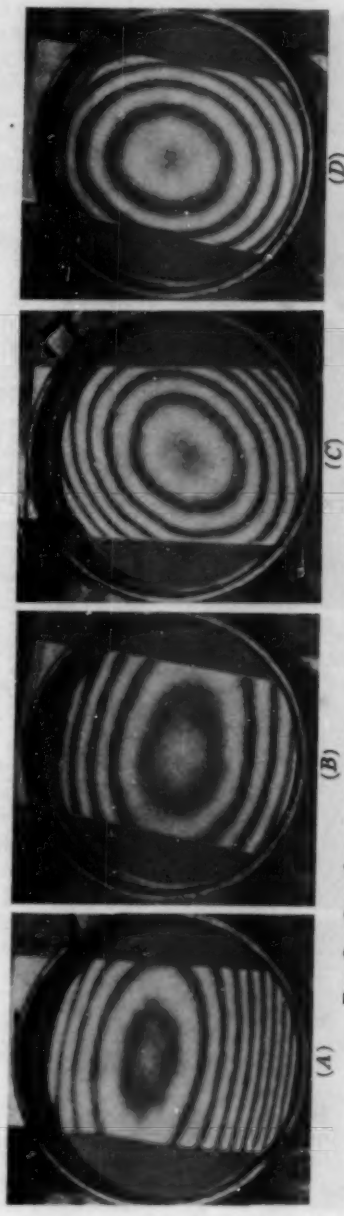

FIG. 3.—Interference patterns on plate glass: (*A*) C; (*B*) D; (*C*) Cr; and (*D*) Dr.

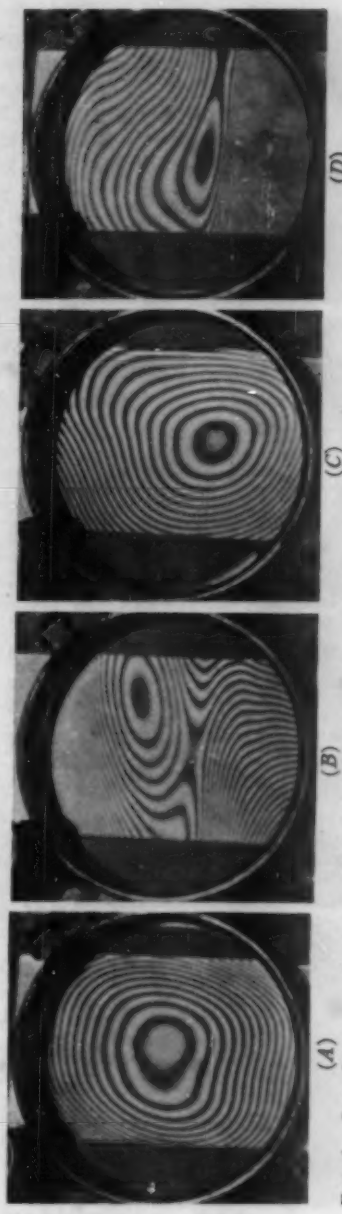

FIG. 4.—Interference patterns on single-strength Pennvernon window glass; (*A*) picture glass A; (*B*) window glass B; (*C*) picture glass Ar; and (*D*) window glass Br.

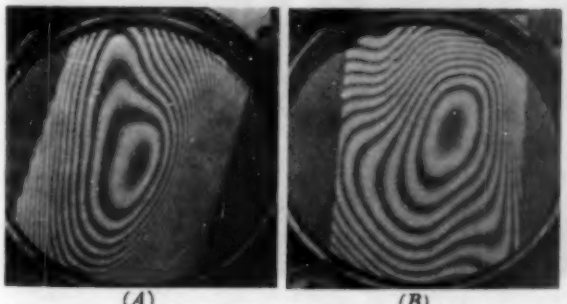

FIG. 5.—Interference patterns on double-strength Lustraglass B; (*A*) front; (*B*) reverse.

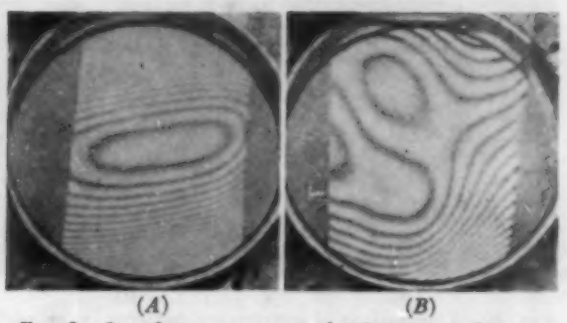

FIG. 6.—Interference patterns of unknown specimens.

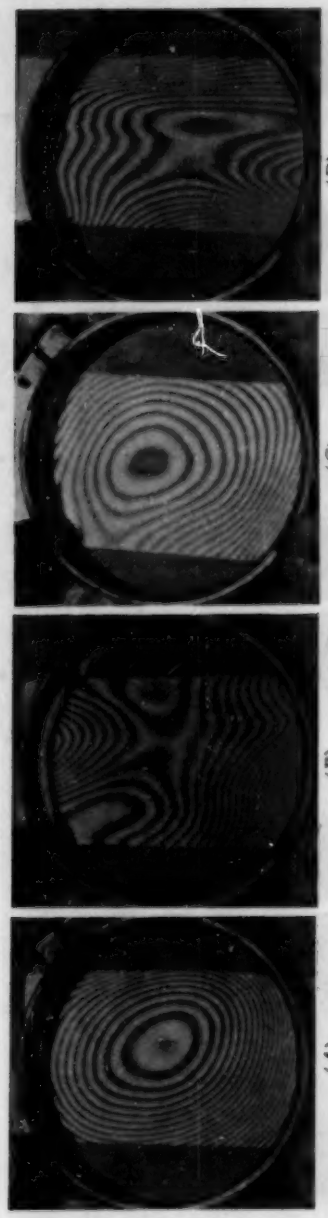

FIG. 7.—Interference patterns on single-strength Lustraglass; (*A*) picture glass A; (*B*) window glass B; (*C*) picture glass Ar; and (*D*) window glass Br.

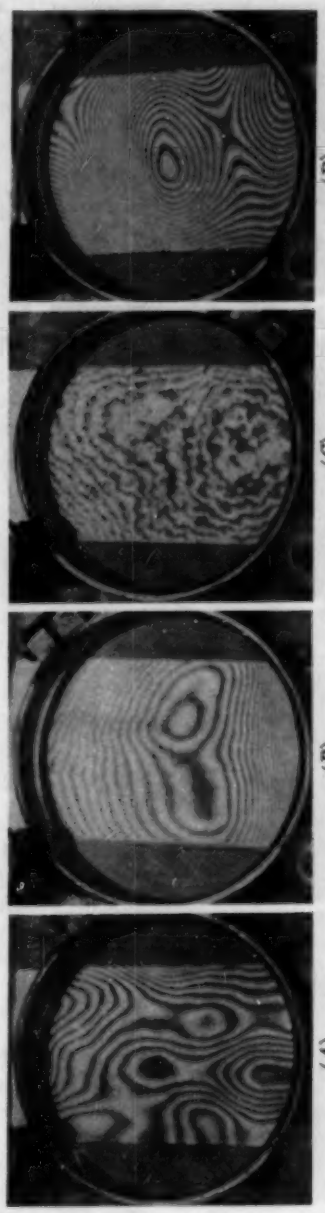

FIG. 8.—Interference patterns on Libbey-Owens-Ford window glass B; (*A*) single strength; (*B*) double strength; (*C*) single strength (reverse); (*D*) double strength (reverse).

FIG. 9.—Interference patterns on double-strength Pennvernon window glass; (*A*) picture glass A; (*B*) window glass B; (*C*) picture glass Ar; and (*D*) window glass Br.

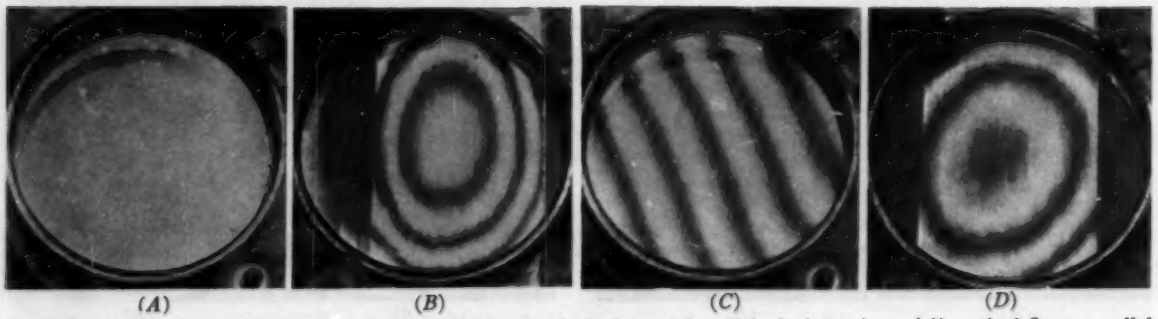

FIG. 10.—Comparison of interference patterns on an optical glass with polished plate glass; (*A*) optical flats, parallel surfaces; (*B*) polished plate glass; (*C*) optical flats, not parallel; and (*D*) polished plate glass (reverse).

graphed on 35-mm. film with the Argus C-2 camera. The camera is placed so that the angle of incidence is approximately 20 degrees. Super-XX film is used, and exposures of about one second are made at f18.

The distance between dark bands in the interference patterns is one half wave length, which amounts to twelve millionths inch in the case of the light used here. By measuring the number of bands in a given distance, for example, the 2-in. diameter of the optical flat, the degree of curvature of the surface may be calculated easily.

Interference patterns of flat glass surfaces disclose certain distinctive features which are related to the method of manufacture, and the previous history of the glass often shows up in a surprising manner. Several useful criteria may be used to distinguish between plate glass and window glass as follows: (1) The number of bands shown by plate glass is always small, whereas the number shown by window glass is usually large; (2) the bands of plate glass are generally circular or elliptical and occasionally hyperbolic; those of window glass trace asymmetrical topographies; and (3) the bands of window glass are generally clear and sharp; those of plate glass show a fuzziness as a result of grinding marks.

III. Types of Patterns

To illustrate the distinctive patterns of various types of flat glass, photographs are shown of a series of commercial samples. Figures 2 and 3 show typical interference patterns for four different samples of plate glass. Because of the nature of the manufacturing process, their differences are not significant in this method of examining plate glass. The samples have therefore been chosen to illustrate the various types of pattern that occur in good commercial plate glass. Patterns of the front and reverse sides of each glass are shown.

An outstanding characteristic of plate glass is that it is very flat, and it will be noticed that these samples fall well within ten bands per inch. The patterns, furthermore, are symmetrical, indicating that such curvature as exists is relatively uniform and regular. Ultramicroscopic vestiges of grinding marks, which have not been removed by polishing, show up in Fig. 2 (*A*) and (*C*), as fuzziness on the edge of the bands. The lack of pattern in Fig. 2 (*D*) indicates planeness approaching an optical flat. The hyperbolic pattern of sample B, Fig. 2 (*B*), is unusual and occurs in plate glass only when it is exceptionally flat.

The patterns in Fig. 3 are considered to be representative of good plate glass.

Three major processes in commercial use for manufacturing window glass are variously known by the names of their inventors or by the trade name under which the glass is sold. The interference patterns of these glasses are affected considerably by the process of manufacture. These glasses, consequently, have been designated to indicate their origins. Commercial-sized sheets, representing each of the three processes of manufacture in single-strength and double-strength window glass and in single-strength picture glass, were purchased from local retail dealers. The interference patterns of representative pieces cut from these sheets were photographed and are shown in Figs. 4, 5, 7, 8, and 9.

The distinctive characteristics of window-glass patterns are evident in these figures. Figure 4 shows that (1) the number of bands per inch is large, (2) the bands trace asymmetrical topographies, and (3) the bands are clear and sharp. In examining drawn sheet glass, however, one of these distinctive characteristics is frequently lacking from one side of a sheet and occasionally from both sides. The examination on both sides is therefore desirable so that positive identification may be based on all of the available evidence. The more nearly symmetrical pattern shown by the picture glass (A-quality window glass), Fig. 4 (*A*), confirms, the judgment of the cutter, but the slight asymmetry and the number and clearness of the bands are convincing evidence that it is drawn sheet. On the samples shown in Fig. 9, the flatness approaches that of plate glass, but the asymmetry proves beyond doubt that a drawn sheet is involved.

An interesting pattern on the sample of single strength (reverse) in Fig. 8 apparently originates at the bending roll in the Colburn process. This effect is also discernible on the pattern of the double-strength glass Fig. 8 (*B*).

The distinctive quality of an optical flat is evident in the patterns in Fig. 10, where it is compared with an excellent sample of polished plate glass. The optical flat, which is adjusted to a parallel alignment with the reference optical flat, shows no bands but merely a single bright area. These flats are accurate to about one eighth of a wave length. If they are not adjusted to be parallel, a series of straight bands indicating the inclination may be obtained. The clearness of these bands is obtained only by the extremely laborious process involved in the production of an optical surface.

Two specimens of unknown origin are presented in Fig. 6; pattern *B* is obviously window glass, and pattern *A* is known to be window glass because of the number of bands per inch and their clearness; this glass has exceptional symmetry.

IV. Use for Large Pieces of Glass

Although this procedure of test has been applied to a study of small specimens of glass to show by interference bands the process by which the glass was produced, it may be readily extended to larger pieces by substituting a ring base for the solid base of the present instrument. The optical flat holder could then be placed directly on the sample under examination and aligned to give the characteristic pattern.

Plate Glass Fellowship
Mellon Institute of Industrial Research
Pittsburgh, Pennsylvania

Forty-Fourth Annual Meeting American Ceramic Society

April 19-25, 1942

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AMERICAN CERAMIC SOCIETY

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JOURNAL REFERENCE: The journal name appears in italics, followed by the volume (bold-faced), issue number (in brackets), page numbers, and year (in parentheses).

November, 1941
20—11

Abrasives

Spark test as a plant control. HAROLD A. MALONEY. *Metal Progress*, **39** [2] 209–11 (1941).—Spark testing is one of the surest and fastest methods of inspecting metal to determine its general composition, the presence of special alloys, and the presence of tramp iron having the same surface appearance. The operator must watch the selection of the grinding wheel, its speed, and the pressure of the steel upon the wheel. The test is preferably carried out in a darkened room. A skilled operator can detect differences of 0.05% carbon in steels with up to 0.30% carbon. As the carbon content increases, the number of explosions appearing in the spark stream increases, and the stream becomes quite bushy. The types of sparks obtained for various steels and steel alloys are described and illustrated. B.C.R.

SEPARATE PUBLICATION

Abrasive Materials. ROBERT W. METCALF. Preprint from U. S. Bur. Mines Minerals Yearbook, Review of 1940. Supt. of Documents, Govt. Printing Office, Washington, D. C. 16 pp. Price 10¢. R.A.H.

PATENTS

Cambering mechanism for grinding machines. C. L. SCHULTE AND A. J. GRAF (Cincinnati Grinders, Inc.). U. S. 2,254,020, Aug. 26, 1941 (Nov. 7, 1938).

Design for tool-grinding machine. R. B. PEALER (Beaver Pipe Tools, Inc.). U. S. 129,177, Aug. 26, 1941 (April 14, 1941).

Diamond dressing tool and method of dressing grinding wheels. J. L. PETRIE (Wheel Trueing Tool Co.). U. S. 2,254,392, Sept. 2, 1941 (Aug. 2, 1940).

Electric indicator for grinding machines. H. J. LOVENSTON (Gear Grinding Machine Co.). U. S. 2,256,120, Sept. 16, 1941 (May 20, 1940).

Grinding or abrading machines. A. SCRIVENER, LTD., AND A. SCRIVENER. Brit. 538,465, Aug. 20, 1941 (April 8, 1940). WRIGHT ELECTRIC MOTORS (Halifax), LTD., AND H. H. WRIGHT. Brit. 538,466, Aug. 20, 1941 (April 9, 1940).

Grinding machine. JACOB DECKER AND HANS ERNST (Cincinnati Grinders, Inc.). U. S. 2,254,002, Aug. 26, 1941 (June 2, 1939). CHARLES HERFURTH AND R. D. WORTENDYKE (Cincinnati Grinders, Inc.). U. S. 2,254,010, Aug. 26, 1941 (April 25, 1938).

Grinding the teeth flanks of spur wheels. H. KOLB. Brit. 538,263, Aug. 7, 1941 (Sept. 1, 1938).

Grinding wheel. CARL WOLF. U. S. 2,256,367, Sept. 16, 1941 (May 16, 1939).

Grinding wheel feeding mechanism. H. A. SILVEN (Norton Co.). U. S. 2,254,784, Sept. 2, 1941 (June 5, 1940).

Honing machine. C. O. HOLLAND (Barnes Drill Co.). U. S. 2,255,583, Sept. 9, 1941 (April 15, 1939).

Honing tool. H. B. BARRETT (Barrett Equipment Co.). U. S. 2,254,508, Sept. 2, 1941 (Aug. 14, 1939).

Hood for attachment to diamond tools. J. L. PETRIE (Wheel Trueing Tool Co.). U. S. 2,254,393, Sept. 2, 1941 (Dec. 24, 1940).

Preserving abrasive-coated material. DUREX ABRASIVES, LTD. Brit. 538,019, July 30, 1941 (Dec. 27, 1938).

Rubber-bonded abrasive article and mix. R. H. MARTIN (Norton Co.). U. S. 2,254,612, Sept. 2, 1941 (Jan. 22, 1940).

Screw thread grinding machine. S. A. HORSTMANN AND HORSTMAN, LTD. Brit. 538,393, Aug. 13, 1941 (July 12, 1939).

Tool-grinding device. J. V. CARLSON (Union Special Machine Co.). U. S. 2,253,687, Aug. 26, 1941 (April 3, 1939).

Waterproof sandpaper. RICHARD P. CARLTON AND BYRON J. OAKES. Can. 398,352, Aug. 5, 1941 (Jan. 31, 1936). G.M.H.

Art and Archeology

Artistic tile oven. R. LUNGHARD. *Keram. Rundschau*, **47** [9] 91–93 (1939).—The modern revival of tile stoves in houses is described and illustrated by examples. M.H.

Bavarian faiences. ANON. *Keram. Rundschau*, **47** [11] 113–15 (1939).—Faience factories were first operated in Bavaria around 1700. Each developed its own characteristic style, particularly with regard to beer pitchers and mugs. Other decorative articles were also made. Illustrated. M.H.

Cooperation between art schools and glass manufacturers. J. C. VIGDEN-JENKS. *Jour. Roy. Soc. Arts*, **86**, 590–605 (April 29, 1938).—The author believes that schools of art should be an essential part of the glass industry. Since 1935, he has conducted a school in Stourbridge which trains three groups of workers: (1) apprentices in glass design and decoration, boys from 12 to 16 years of age; (2) young designers who supplement studio work with actual production at the furnace and in the decorative workshops; and (3) designers or craftsmen already in the industry. The present high position of the school is due largely to its own initiative and that of an energetic committee supported by the glass industry. The entire town is justly proud of its famous lead-crystal glass. The glass batch is composed of silver sand 4 parts, red lead 3 parts, potash 2 parts, and saltpeter 1 part; it is melted in a furnace capable of maintaining a working temperature of about 1350°C. The batch is placed in crucibles or pots having open mouths easily accessible from the front of the furnace and capable of containing up to 15 cwt. of batch; these are usually arranged in batteries of 8, 10, or 12 to a circular furnace. The intense heat required to reduce this material to molten glass is generally supplied by producer gas. The pots used are made of the special clay for which Stourbridge is famous all over the world. The furnace, once fired, must work continuously day and night, year in and year out. The story of how the school secured an efficient glassmelting furnace is told, and the organization of a full time Junior Art Department, engaged in various forms of general and specialized art education, is described. K.R.

Decoration of faience vessels. MICHAEL BIRKENBIHL. *Keram. Rundschau*, **47** [35] 389–92; [37] 412; [38] 417–21; [40] 438–39; [42] 455–57; [44] 474–76 (1939).—B. presents a historical sketch of faience art which was first developed in Spain in the early middle ages by the Moors. At the beginning of the 15th century, Italy took a leading position, and the art spread to France, Germany, and northern Europe. Many famous pieces of this art are mentioned. Some of them are described, and a few are reproduced. M.H.

Dehydration of aqueous pigment pastes. O. J. SCHIERHOLTZ. *Can. Chem. & Process Industries*, **23** [8] 401–404 (1939).—Experiments were performed with iron blues to find a nonaqueous volatile liquid which could be evaporated from pigments without causing caking. When a water-oil emulsion of the blue, using petroleum thinner (boiling range 160° to 210°C.) as the oil phase, was added through a water-cooled nozzle to a body of the solvent at about 100°C., the globules of aqueous blue from the emulsion dehydrated as separate units. There was then no tendency toward coalescence. Coconut oil diglyceride was used as an emulsifying agent. When all water had been removed by distillation, the pigment was separated by decantation and filtration. The oven-dried product was a fine, soft powder with rich, pure color and low hygroscopicity (2.8%) and could be readily ground. Wettability was so low that a petroleum suspension of the blue could be shaken with water to wash out soluble salts. B.L.

Engobes, glazes, and oxide colors for art ceramics. ANON. *Keram. Rundschau*, **47** [8] 75–77; [10] 103–105 (1939).—The various techniques of decorating with engobes, colors, and glazes are surveyed and discussed. Illustrated. M.H.

Excavations in Uzbekistan. HENRY FIELD AND EUGENE PROSTOV. *Asia*, **41**, 242–44 (1941).—Barrows excavated near Kaunchi-Tepe are assignable to three epochs. One was a burial containing a flat-based wide-necked vessel, handmade and only slightly fired. This was of the late Bronze Age. A group interment was found which contained narrow-necked vessels, flat plates, and pear-shaped jugs. These were well fired, and some were covered with a red slip. The date was about 500 B.C. Catacombs with many bronze objects and earthenware pitchers, made on the wheel and well fired, were located; these were about A.D. 300 to 400. At Kara-Tepe, an ancient Buddhist monastery with frescos was found. Airtam yielded many different kinds of pottery; pottery kilns and heaps of slag indicated extensive development of pottery manufacture. During construction of the Ferghana canal many ancient sites were found. On these sites, crude, handmade pottery, dishes, jugs, and burnished ware were located. Ninety-two adjacent sites were discovered. At one place, an unbroken cultural stratum extends for 8 km. See "Soviet. . . ," *Ceram. Abs.*, **19** [8] 181 (1940). W.D.F.

Five early Chinese pagodas. LIANG SSU-CH'ENG. *Asia*, **41**, 450–53 (1941).—In Sung Shan, Honan province, is a brick pagoda with twelve sides and fifteen stories; it was built in A.D. 523. It shows Indian influence. A single story stone pagoda located 30 miles south of Tsinan, Shantung, was built in A.D. 544. A seven-storied brick pagoda in Sian was built in A.D. 652 and wasreb uilt in A.D. 705. A wooden pagoda, 50 miles south of Ta-t'ung, Shansi, was built in A.D. 1056. The "Flower Pagoda" on the Peiping-Hankow railroad in Hopeh province is octagonal with hexagonal chambers attached on four alternate walls of the octagon. It was built of brick in the 12th century. W.D.F.

Glazes for stoneware and faience. ERNST HINRICHS. *Keram. Rundschau*, **47** [37] 410–11; [39] 429–31 (1939).—H. describes the production of a new series of stoneware and faience and the furnace used. Two glazes for stoneware were used: (1) 189.04 parts by weight of feldspar, 2.58 parts kaolin, and 66 parts marble powder, with the following Seger formula:

$$\left.\begin{matrix}0.34\ K_2O\\0.66\ CaO\end{matrix}\right\}\ 0.35\ Al_2O_3\qquad 2.06\ SiO_2$$

(2) 150.12 parts by weight of feldspar, 69.66 parts kaolin, 73 parts marble powder, and 26.40 parts quartz powder, with the following Seger formula:

$$\left.\begin{matrix}0.73\ CaO\\0.27\ K_2O\end{matrix}\right\}\ 0.54\ Al_2O_3\ \ 2.60\ SiO_2$$

The faience body was made of 700 parts by weight of red-firing Westerwald clay, 200 parts red-firing Löwenberg clay, 100 parts coarse quartz sand, and 200 parts chalk; the mass was prepared in drum mills for 35 hr. and fired to Seger cone 07*a*. The mat glaze for this material was, after several experiments, composed of a frit of 57.3 parts by weight borax, 15.0 parts chalk, 159.6 parts red lead, 120.0 parts quartz powder, 46.7 parts zinc oxide, and 15.9 parts tin oxide; the mill addition consisted of 100 parts frit, 10.0 parts zinc oxide, 5 parts tin oxide, and 6.0 parts kaolin. The Seger formula is as follows:

$$\left.\begin{matrix}0.073\ CaO\\0.073\ Na_2O\\0.342\ PbO\\0.512\ ZnO\end{matrix}\right\}\ 0.043\ Al_2O_3\ \left\{\begin{matrix}1.064\ SiO_2\\0.146\ B_2O_3\\0.114\ SnO_2\end{matrix}\right.$$

For coloring effects, additions of 6 parts by weight of rutile gave a cream-colored mat glaze; 0.3 part nickel oxide, a delicate steel blue; 2 parts copper oxide and 0.2 part nickel oxide, a bright green glaze; 2 parts uranium oxide, a chamois-colored mat glaze; 1 part cobalt oxide and 1.4 part copper oxide, mat blue; 6 parts copper oxide, 4 parts manganese oxide, 2 parts cobalt oxide, and 2 parts black color substance, a dull black glaze; 1.2 parts antimony oxide and 0.5 part copper oxide, light green; and 0.6 part copper carbonate, a light turquoise. Variations which produce different artistic effects are presented. M.H.

Great ceramics of China. ANON. *Art News*, **40** [11] 20–21 (1941).—The Buffalo Museum of Science is showing "Three Thousand Years of Chinese Ceramics" in connection with the national appeal for United China Relief. Talks were given by Henry R. Luce and Dr. Chih Meng of China Institute. The exhibit covers the period 2000 B.C. to A.D. 1280. Pottery was an advanced art in China by 2000 B.C., and Neolithic ceramic tripods were probably models for the first bronze casters. There were also finer examples for funerary and general use; these were wheel turned, kiln fired, and painted with floral motifs relating to Russia and the Near East. From 1766 to 255 B.C. bronze repaid the debt to ceramics, and pottery became the cheap substitute for the metal vessels. During the Han dynasty (206 B.C.) terra-cotta figures of humans, manlike deities, and playful beasts were placed in the tombs, Egyptian fashion. Buddhism brought an Indian influence during the Wei and Sui periods (A.D. 221 to 618). The golden age of T'ang (618 to 907) brought rich colorings to glazes, and at this time porcelain was perhaps accidentally evolved from kaolinic earth and petuntse. In the Sung age (960 to 1280) high-fired stoneware and porcelain predominated; they were decorated with rich incised patterns and soft-toned glazes. Illustrated. M.E.P.

Liverpool pottery for the American market. H. BOSWELL LANCASTER. *Connoisseur*, **107** [477] 208–209 (1941).—Pottery manufacturers took advantage of their seaport location to establish an export trade with America as early as 1710; the ware was delft with a white glaze and simple coloring of blue, puce, yellow, and green. With transfer printing (1752) and creamware, appeared jugs with pictures of ships, naval celebrities, and flags. A special design or mark of the American eagle with the words, Herculaneum Pottery, Liverpool, seems to have been used for pieces intended for the American market. The sailors' departure and return were the inspiration of many figures and groups by the Woods and others. The manufacture of pottery in Liverpool ceased about a century ago. Illustrated. M.E.P.

Living arts of the Indians. RENÉ D'HARNONCOURT. *Magazine of Art*, **34** [2] 72–77 (1941).—The Indian exhibit at the Museum of Modern Art traces art development in the U. S. and Alaska. Grouped in three main sections it covers (1) Indian art before discovery of the different tribes by Europeans, called the Section of Prehistoric Art; (2) historic and contemporary tribal art, called the Living Tradition; and (3) a smaller group of contemporary work especially suited to the 20th century, called Indian Art for Modern Living. Prehistoric pottery from the Southwest is illustrated with a food bowl on which is painted, in the highly individual style of the Mimbres culture, a warrior decapitating his foe. A pottery doll representing a woman of the Mohave tribe, Arizona, is illustrated. The visitor's main impression of the prehistoric section, however, will be of a collection of sculpture and ceramics displayed with classic simplicity in severe white-walled rooms. Illustrated. M.E.P.

Methods of decorating glassware: I, Altering the glass surface. ANON. *Ceram. Ind.*, **37** [1] 30–34 (1941). —Methods of decorating glass by changing the surface of the glass are described. These are (1) engraving or cutting, (2) sandblasting, (3) glue chipping, and (4) acid frosting and etching. Illustrated. H.T.

Preparation of gold luster for pottery. ANON. *Keram. Rundschau*, **47** [26] 293–94 (1939).—The preparation of gold luster is described. It is composed of 20 gm. gold resin (equal to 12 gm. Au) which is dissolved in 24 gm. rosemary oil and 12 gm. fennel oil over a water bath at 50°C. When it is completely dissolved, 2 gm. rhodium solution, 9 gm. bismuth solution, 1 gm. chromium solution, 17 gm. asphaltum solution, and 15 gm. colophony solution are added. After the solution has been shaken thoroughly for some time, it is ready for use. The preparation of the various solutions is described in detail. M.H.

Rare pair of Ming blue and white vases. HELEN COMSTOCK. *Connoisseur*, **107** [477] 212 (1941).—An exceptionally fine pair of baluster vases of the Hsüan Tê period (1426–1435) has been acquired by the Nelson Gallery of Art in Kansas City, Mo. They are 21 in. high and are a true pair, with the design reversed. The pure tonality of the early Ming blue and white was especially admired by the Chinese and was the result of the high quality of ore which was at that time imported from Persia. Later, as the supply was interrupted, inferior ores were used; these produced at times a more brilliant tone but one not so pure in quality. The glaze is slightly bluish and has the "orange-skin" texture. Illustrated. M.E.P.

Technical production of Chinese porcelains: I. W. FUNK. *Ber. Deut. Keram. Ges.*, **22** [5] 163–93 (1941).—The entire collection of Chinese porcelains has been moved to its new location in the Zwinger State Porcelain Gallery. F. describes the production and decoration of the old Chinese porcelains, the literature on which is only difficultly accessible. According to old Chinese writings, the first porcelain was made at the end of the 6th century, though the oldest known fragments from Samarra on the Tigris are ascribed to the years 838 to 883. In the course of at least a thousand years, there have been fewer changes in the production of porcelain than in its decoration. The production of the white, undecorated porcelain is described in Part I, while its decoration with colored glazes and painting will be considered in Part II. Language difficulties and lack of knowledge of the Chinese themselves make it difficult to obtain exact information. In the 19th century, the chemists of the Sèvres porcelain works first examined the Chinese raw materials for porcelain. Results were published by J. J. Ebelmen and A. Salvétat in 1850 and by St. Julien in 1856. About 50 years later Vogt, director of the Sèvres porcelain works, brought out a more comprehensive report based on a publication of the French Consul F. Scherzer and a collection of specimens which Scherzer had gathered in the province of Kiang-si. Vogt's report, therefore, does not necessarily apply to other times and localities. In China, as elsewhere when porcelain is made, there is need of an earthy material of loose structure and of a solid hard mineral material. F. assumes, as did Salvétat, that both main constituents of porcelain occurred together in the mountain Kao-ling, which was a source of raw materials and gave the name to kaolin. According to G. Vogt, the raw materials used in 1882 were as follows: (1) porcelain earth (kaolin), which contained, in the plastic part which was soluble in sulfuric acid, kaolin ($2SiO_2 \cdot Al_2O_3 \cdot 2H_2O$) and considerable white mica ($6SiO_2 \cdot 3Al_2O_3 \cdot K_2O \cdot 2H_2O$) in very fine particles; (2) hua-schi, a material regarded as porcelain earth, which contained much fine white mica and a little feldspar and quartz; and (3) petun and you-kuo, which are the fluxes; they are not the same as the European pegmatite and feldspar but consist of quartz and white mica and contain only a little feldspar. Vogt concluded that the hua-schi of one firm was composed of $^1/_3$ white mica and $^2/_3$ kaolinite, while the hua-schi-tse (used for slip painting) contained 95.85 parts of a similar mixture and 4.15 parts of quartz. The hua-schi of another firm was composed of 12.08 white mica, 68.46 kaolin, 11.84 orthoclase, and 7.30% quartz. The composition of the soluble part of the you-kuo is very close to the theoretical composition of muscovite. Tests of three samples of the insoluble part of you-kuo gave the following composition: quartz 52.9 to 56.5, white mica 30.2 to 31.4, feldspar (albite) 11.0 to 13.4, silicic acid 0.0 to 1.0%, calcium carbonate 1.9 to 2.3%. Tun was a raw material intermediate between porcelain earth and the easily melted you-kuo and was of variable composition as shown by the following table.

Sample	1	2	3	4	5
Quartz (%)	53.8	46.8	45.2	42.4	35.3
White mica (%)	40.6	37.3	31.3	26.0	18.9
Feldspar (%)	5.6	15.9	23.6	31.6	45.8

The feldspar was mainly albite. Raw materials were prepared near their source, especially if water power was available. The porcelain earth was purified by mixing with water and drawing off the earth suspended in the water. The earth was placed in porous bags, the water was re-

moved by pressure, and the remaining earth was made into cakes which, when dried, were delivered to the porcelain works. The harder materials, tun and you-kuo, had to be ground to powder in stamp mills by water power. Afterward, the preparation was similar to that of the porcelain earth. The raw materials often required further purification after delivery at the porcelain works. The raw materials were mixed in different proportions depending upon the ware to be made; e.g., for fine porcelain, equal amounts of porcelain earth and pei-tun-tse were used. Pei indicates that the material is white, and tse signifies a diminutive. For moderately fine ware, 2 parts of earth and 3 parts of pei-tun-tse were used, while for inferior bodies, only 1 part of earth and 3 parts of pei-tun-tse were used. Vogt has calculated the mineralogical composition of the bodies used by various plants as follows:

Plant	Quartz (%)	Feldspar (%)	Kaolinite (%)	White mica (%)
Ho	30.68	14.82	30.08	24.49
Li	34.69	16.49	22.51	26.56
Imperial	28.0	25.0	23.5	23.5
Lin	30.8	19.4	31.8	18.0

The Lin body differs from the others in the use of hua-schi in place of kaolin. That the Chinese bodies show a remarkable similarity not only between different plants but also between different periods is illustrated by the following analyses of fired porcelain:

	Old celadon body (%)	Body of 1850 (%)	Body of 1890 (%)
SiO_2	69.51	69.0	69.50
Al_2O_3	22.72	23.6	23.10
Fe_2O_3	1.84	1.2	2.00
CaO	0.27	0.3	0.16
MgO	0.36	0.2	0.22
K_2O	4.79	3.3	3.72
Na_2O	0.87	2.9	1.28

The fact that such uniformity could be maintained, without scientific help, over a period of one or two hundred years is remarkable and shows that the Chinese are very skillful craftsmen. The general Seger formula may be given as $15.0\ SiO_2 \cdot 3Al_2O_3 \cdot RO$, where R consists in varying proportions of Na, K, Ca, or Mg. The firing temperature of this body lies around 1270°C. According to Vogt, the special characteristics of the oriental porcelains, e.g., that they may be decorated with relief enamel, is due to their being fired 100°C. lower; the chemical composition of the Chinese bodies does not differ from that of the bodies of most European plants. There is a possibility that the Chinese bodies do not require as high a firing temperature because the constituents are more intimately mixed in nature. W.H.H.

BOOK

Pottery in the United States. HELEN E. STILES. E. P. Dutton & Co., Inc., New York, 1941. 529 pp., 132 illustrations. Price $3.00.—S. presents a rich store of information on the art of ceramics in America. With the same fine integrity which marked her work in her previous books, the story of the earliest importations from China and England is given with amusing and entertaining anecdotes concerning backgrounds. Symbolism, as used by the early designers, and the decorative mottoes which figured so prominently in all household ware of the 17th and 18th centuries in America are treated.

Collectors of Bennington ware will enjoy the description of its early popularity. There is a section on White House china. Parallel with the story of our early American taste in china and pottery, S. gives an amusing commentary on the American way of life. The story is told of the first stationary bathtub, which made its appearance in Cincinnati in 1842, followed by an engaging description of its modern counterpart. Modern china is discussed in detail, and an interesting account of modern tile and their uses is presented. Photographs of exceptional clearness and beauty and many line drawings illustrate the book. A comprehensive bibliography is included. This is a valuable addition to the library of every American who is interested in the pottery of our own land.

S. was born in Norristown, Pa., and educated at Penn State College, the University of Pennsylvania, and Columbia University. She is a teacher and lives in Kent, Ohio. Her research in her favorite field has taken her to the doors of the great museums both in Europe and America. This book is the fourth in a series, all well written and based on careful research. The other three are "Pottery of The Ancients" (*Ceram. Abs.*, **17** [9] 297 (1938)), "Pottery of the American Indians" (*ibid.*, **18** [11] 290 (1939)), and "Pottery of the Europeans." S. shows in her writings that she has material much in excess of what she could use. She has used remarkable judgment in her restraint. Time and space limited but did not cramp her writings. This is indeed a remarkable book.

R.C.PURDY

PATENTS

Decalcomania. F. W. HUMPHNER (Mid-States Gummed Paper Co.). U. S. 2,254,428, Sept. 2, 1941 (Dec. 29, 1938; June 16, 1939).

Designs for:

Bottle. B. D. FUERST (Owens-Illinois Glass Co.). U. S. 129,163, Aug. 26, 1941 (Jan. 9, 1941).

Chinaware or earthenware. PARAGON CHINA, LTD. Can. 13,116 and 13,117, July 14, 1941. G.M.H.

Coffee cup. ALBERT TUJAGUE (Loubat Glassware & Cork Co.). U. S. 129,496, Sept. 16, 1941 (April 26, 1941).

Combined range and kitchen heater. E. D. PELLEGRIN (Geo. D. Roper Corp.). U. S. 129,467, Sept. 9, 1941 (March 24, 1941).

Combined top and back splash panel for ranges. E. D. PELLEGRIN (Geo. D. Roper Corp.). U. S. 129,462, Sept. 9, 1941 (March 24, 1941).

Gas range. E. D. PELLEGRIN (Geo. D. Roper Corp.). U. S. 129,463 and 129,464, Sept. 9, 1941 (March 24, 1941).

Glass jar. W. J. LUNDY (Olean Glass Co.). U. S. 129,509 and 129,510, Sept. 16, 1941 (July 22, 1941).

Jar. H. M. GEHM (Owens-Illinois Glass Co.). U. S. 21,900, Sept. 16, 1941 (July 24, 1941); reissue of original U. S. 126,977, May 6, 1941 (March 24, 1941).

Range. E. D. PELLEGRIN (Geo. D. Roper Corp.). U. S. 129,465 and 129,466, Sept. 9, 1941 (March 24, 1941).

Low-melting decorative glaze of increased resistance to chemical agents. A. J. DEYRUP (E. I. du Pont de Nemours & Co.). U. S. 2,255,044, Sept. 9, 1941 (Jan. 13, 1939).—A low-melting lead glaze maturing below 1200°F. and containing at least 25% by weight of lead oxide, the glaze composition comprising 0.25 to 3% by weight of a halogen selected from the group which consists of chlorine, bromine, and iodine.

Cements

Evaluating a pozzuolana. H. McC. LARMOUR, E. L. McMASTER, AND WM. JAQUES. *Rock Products*, **44** [3] 52–56, 87 (1941).—Increasing use of pozzuolana Portland cements has necessitated the study of the relative merits of pozzuolanas. The strength, which is lowered at early periods for Portland pozzuolana cement mortars and for concrete when normal curing temperatures prevail, can be increased decidedly by finer grinding of the cement. The

pozzuolanic action of silicates is influenced by the chemical composition and the curing temperature. Silicates having a low or negligible amount of alumina are slowly reactive at normal curing temperatures but are highly reactive at elevated ones. Siliceous materials containing high R_2O_3 contents do not show as concordant results between solubility and mortar strengths as siliceous materials with lower R_2O_3 contents. Grinding the pozzuolanas removes surface films from the particles and greatly accelerates activity. The desirable fineness of the selected pozzuolanas may be determined for any curing temperature by an outlined test for activity. B.C.R.

Iron oxide versus alumina as a fluxing agent. ALTON J. BLANK. *Rock Products*, **43** [11] 47–50 (1940).—Data obtained over a three-year period showed that cements having a lower Al_2O_3/Fe_2O_3 ratio were considerably superior to those having a higher ratio. Improvements include gradually diminishing amounts of free lime, increased soundness, higher specific gravity, lower Le Châtelier expansion, and marked improvements in tensile strength at all ages. B.C.R.

Oxides extracted in Merriman's test of Portland cement. E. P. FLINT AND P. H. BATES. *Rock Products*, **43** [10] 46–47 (1940).—The results obtained in applying the Merriman sugar test to a number of cements are reported and discussed. With only a few exceptions, all the constituents in the cement dissolved out partially, and no great preferential solution of any one constituent occurred. Compounds dissolving out and listed in order of decreasing amounts were lime, alumina, silica, iron oxide, sodium and potassium oxides, magnesia, and sulfur trioxide. B.C.R.

Particle-size distribution. F. O. ANDEREGG. *Rock Products*, **43** [9] 52–54 (1940).—Although the hydration reaction of Portland cement occurs only on the surface of the grains and the strength developed depends upon the surface exposed, the unhydrated cement serves as an aggregate, constituting the best available. A proper balance between the cement available for hydration and that left unhydrated is needed. A study of the effect of the size distribution of particles indicated that equal fractions in the ranges 2.5 to 5, 5 to 10, 10 to 20, 20 to 40, and 40 to 80 microns gave the highest strength, densest mortar, and the lowest volume change. The compressive strength was found to be proportional to the specific surface of the cement. The coarser sizes of Portland cement made a much better aggregate than silica. Grinding the coarser clinker particles finer should give an all-around better performance per unit cost. B.C.R.

Potassium sulfate in cement clinker. G. L. KALOUSEK, C. H. JUMPER, AND J. J. TREGONING. *Rock Products*, **44** [4] 52–54 (1941).—Aqueous solutions filtered from mixtures of ground Portland cement and water were analyzed; they showed wide differences in the amount of alkali and sulfate among the 12 clinkers studied. Correlation of K_2O and SO_3 indicated that K_2O is present in many clinkers as the sulfate; this accounts for the large fraction of the total K_2O found in solution. The decreases with time in the concentration of the SO_4 of the solutions in contact with the hydrating clinker indicated that tricalcium sulfoaluminate was precipitated. B.C.R.

Relationship of the garnet-hydrogarnet series to the sulfate resistance of Portland cements. E. P. FLINT AND LANSING S. WELLS. *Jour. Research Nat. Bur. Standards*, **27** [2] 171–80 (1941); RP 1411. Price 5¢.—Experiments on the constituents and on the possible hydration products of Portland cement indicate that the sulfate resistance of Portland cement should be increased by any method resulting in the removal from the set cement of tricalcium aluminate hexahydrate which is unstable in sulfate solutions and substitution for the aluminate of hydrogarnets containing iron or silica, which are stable in such solutions. The substitution may be brought about by (1) reaction of the hydrated aluminate with silica from the various silicates in the set cement, (2) addition of a pozzuolanic material to the cement, and (3) increasing the glass and tetracalcium aluminoferrite contents of the cement. Preparations having an X-ray structure nearly identical with that of grossularite garnet resulted when mixtures of beta-dicalcium silicate, lime, and dehydrated kaolin and of tricalcium silicate and dehydrated kaolin were steamed at 500°C. at 420 atm. R.A.H.

Enamel

Adhesion of enamels to iron. J. WHITE. *Proc. Inst. Vitreous Enamellers*, **4**, 50–63 (1938); see *Ceram. Abs.*, **17** [11] 347 (1938); "Oxidation . . .," *ibid.*, **18** [11] 291 (1939). A.B.

Agitating for uniform enamel coats. ANON. *Ceram. Ind.*, **37** [1] 48–49 (1941).—At the Wrought Iron Range Co., St. Louis, Mo., a 550-gallon enamel storage tank has been installed to save millroom labor, decrease losses, and increase uniformity of sprayed coat. Two pressure cans are used for each spray booth, and specific gravity measurements on their contents are taken every hour. The thickness of the enamel coat is tested by means of an electric thickness gauge. Illustrated. H.T.

Analysis of cast iron for enameling. H. COWAN. *Proc. Inst. Vitreous Enamellers*, **4**, 127–47 (1938); see *Ceram. Abs.*, **18** [8] 203 (1939). A.B.

Australian foundry practice, with special reference to vitreous enameling. W. THOMAS. *Proc. Inst. Vitreous Enamellers*, **4**, 90–126 (1938); see *Ceram. Abs.*, **18** [8] 203 (1939). A.B.

Barium-containing enamels and their toxicity. F. BENESCHOVSKY. *Keram. Rundschau*, **49** [1] 5–7 (1941).—Barium carbonate is now often used to replace boron and lead in enamels, especially in majolica enamels. Great care should be taken in its application, however, as all soluble Ba compounds are extremely poisonous. If Ba is used in enamels on kitchenware, only those frits which are sufficiently acid resistant and give off only traces of Ba should be used. Two compositions for a ground enamel are as follows:

Ground A		Mill addition	
Borax	6.0	Ground A	100.0
Barium carbonate	15.8	Clay	7.0
Quartz	34.0	Quartz	10.0
Feldspar	10.0	Soda	0.5
Soda	19.0	Magnesia	0.1
Saltpeter	6.0	Ground to 8 cm.² residue on a 3600-mesh sieve.	
Fluorspar	8.0		
Cobalt oxide	0.3		
Nickel oxide	0.4		
Manganese oxide	0.5		
	100.0		

Lactic and acetic acids (5%) dissolve not more than 2.24 mgm. BaO per 1 dm.² surface.

Ground	B	C	Mill addition	
Sioglur 5001 Ba	48.0		Ground B	50.0
Feldspar	25.5	50.0	Ground C	50.0
Quartz	11.0	15.9	Clay	7.0
Soda	7.1	24.7	Quartz	10.0
Saltpeter	4.2	1.7	Soda	0.5
Silico-sodium fluoride		2.2	Magnesia	0.1
Fluorspar	3.8	5.3	Ground to 8 cm.² residue on a 3600-mesh sieve.	
Cobalt oxide	0.4	0.2		
	100.0	100.0		

A maximum of 1.44 mgm. BaO was dissolved by lactic and acetic acids. M.H.

De-enameling. ANON. *Keram. Rundschau*, **47** [28] 310–11 (1939).—The enamel layer can be removed from rejects or defective pieces in such a manner that (1) the shape of the piece is retained so that it can be re-enameled or (2) the form of the piece is destroyed, and the material can be used again as scrap in the cupola furnace; the latter is the most simple. In the first case, the enamel can be removed by sandblasting, but this is applicable in practice only to very thick-walled material, storage tanks, etc., under a pressure of 5 to 6 atm. For sheets, etc., only chemical dissolution is practicable; for this, HF of 61 to 65%, diluted to 1:1 to 1:4 (acid:water), is ordinarily used. A 1:1 dilution removes the enamel layer in 20 min.; with a 1:4 dilution, the layer is removed in about 2 hr. The reaction is as follows:

$$12HF + 3SiO_2 \rightleftharpoons 3SiF_4 + 6H_2O$$
$$3SiF_4 + 4H_2O \rightleftharpoons H_4SiO_4 + 2H_2SiF_6$$

For the removal of 1 kgm. of enamel, 1 kgm. of 65% HF is required. The price of HF determines the value of the de-enameling process. M.H.

Estimating, costing, and accounting. W. H. WHITTLE. *Proc. Inst. Vitreous Enamellers*, **4**, 181–98 (1938); see *Ceram. Abs.*, **18** [8] 204 (1939). A.B.

Eutectic enamels. Eutectic viewpoint in the manufacture of boron-free enamels. FRIEDRICH HEIMES. *Sprechsaal*, **73**, 257–59, 267–68, 273–75, 281–83, 289–91 (1940); abstracted in *Chem. Zentr.*, **1940, II**, 2360.—Batch diagrams are given, and their use in the production of boron-free cover enamels is illustrated by an example of a majolica enamel and a sheet cover enamel. An example of a boron-free majolica enamel for cast iron illustrates the narrow limits of the composition of these enamels in contrast with the wide limits of a sheet enamel. H. shows that a great number of easily fusible glazes can be made but that it is more difficult to greatly lower the expansion. The production of boron-free ground enamel cannot be hindered by the lack of suitable glass flux. The difficulties encountered must be regarded as a result of marginal surface reactions with the iron. M.V.C.

Evolution of enameling. W. E. BENTON. *Proc. Inst. Vitreous Enamellers*, **4**, 29–49 (1938); see *Ceram. Abs.*, **17** [11] 348 (1938). A.B.

Firing of vitreous enamels on glass. H. L. CROOK. *Proc. Inst. Vitreous Enamellers*, **4**, 64–73 (1938); see *Ceram. Abs.*, **18** [8] 206 (1939). A.B.

Molding sands and facings. H. MCNAIR. *Proc. Inst. Vitreous Enamellers*, **4**, 167–80 (1938); see *Ceram. Abs.*, **18** [10] 265 (1939). A.B.

Optical aids to the enameling industry. A. H. WILLOUGHBY. *Proc. Inst. Vitreous Enamellers*, **4**, 74–89 (1938); see *Ceram. Abs.*, **18** [8] 204 (1939). A.B.

Smelting boron-free enamels. H. LANG. *Glashütte*, **71** [13] 195–96 (1941).—The difficulties which must be overcome in the production of satisfactory enamels without boron compounds are as follows: (1) the high viscosity of the melt; (2) the brittleness of the smelted enamel; (3) the very short time and temperature interval between the softening point and the melting point; (4) the poor dissolving capacity for metal oxides and coloring substances; (5) the difficulty of obtaining sufficient preliminary opacification. M.V.C.

Thin coating, high temperature increase enamel strength. E. W. DIETTERLE. *Ceram. Ind.*, **36** [6] 62 (1941).—D. gives a short description of an apparatus for measuring the cross-bending strength of enamel. He concludes that, in ground coat enamels, the greatest elasticity is produced by a long firing time and thin application. H.T.

Transfers for vitreous enameling. MECRATE-BUTCHER. *Proc. Inst. Vitreous Enamellers*, **4**, 149–66 (1938); see "Evolution . . .," *Ceram. Abs.*, **18** [7] 174 (1939). A.B.

PATENTS

Abrasive equipment. V. E. MINICH (American Foundry Equipment Co.). U. S. 2,254,234, Sept. 2, 1941 (Oct. 9, 1933; renewed April 7, 1939).

Enameling furnace. A. J. BOLAND. U. S. 2,256,275, Sept. 16, 1941 (Nov. 18, 1939).

Enamel removing means. C. C. RHODES. U. S. 2,256,-267, Sept. 16, 1941 (June 8, 1939).

Enamelware. TITANIUM ALLOY MFG. CO. Brit. 538,-224, Aug. 7, 1941 (Nov. 10, 1938).

Production of opacifiers for vitreous enamels. TITANIUM ALLOY MFG. CO. Brit. 538,223, Aug. 7, 1941 (Nov. 1, 1938).

Glass

Canada starts an optical glass industry. ANON. *Glass Ind.*, **22** [8] 335–39 (1941).—Research Enterprises, Ltd., on July 8, dedicated its new $7,000,000 plant for all stages of optical instrument manufacture up to final assembly. 25 photographs. A.P.

Chemical stability of Russian optical glasses. V. S. MOLCHANOV. *Optiko Mekh. Prom.*, **11** [2] 3–7 (1941).—A series of optical glasses manufactured in Russia was tested with regard to their water and acid stability. The results of tests are tabulated. See "Conductometric . . .," *Ceram. Abs.*, **19** [6] 136 (1940); "Use . . .," *ibid.*, **20** [8] 192 (1941). M.V.C.

Colloidal graphite. BERNARD H. PORTER. *Can. Chem. & Process Industries*, **23** [3] 124 (1939).—The ability of colloidal graphite to lubricate in the presence of heat has resulted in its use in casting glassware. Other special properties are its opaqueness and blackness, ability to remove residual gases from evacuated systems, and variable electrical conductivity. All characteristics of colloidal graphite may be imparted to porous bodies impregnated with it. See "High-Temperature . . .," *Ceram. Abs.*, **18** [10] 275 (1939). B.L.

Color. BRUNO SCHWEIG. *Glass*, **18** [7] 198–204 (1941).—As an introduction to a study on colored glass, S. discusses such terms as color, color vision, colored substances, and chemical constitution. B.C.R.

Colored glass containers protect light-sensitive pharmaceuticals. ANON. *Ceram. Ind.*, **37** [1] 40–42 (1941).—Several light-transmission curves are shown for glass-container compositions. Among commercial glasses, there is a range of absorption curves available which, if properly chosen, will be protective for light-sensitive drugs. H.T.

Effect of chemical durability of glass on the asymmetry potential and reversibility of the glass electrode. EDGAR H. HAMILTON AND DONALD HUBBARD. *Jour. Research Nat. Bur. Standards*, **27** [1] 27–32 (1941); RP 1400. Price 5¢.—The outer surface of the bulb of a glass electrode is attacked appreciably when immersed in alkaline solutions of pH greater than about 9. As a marked voltage departure proportional to the rate of attack occurs in this region, it is reasonable to assume that the voltage departure is a result of the attack and depends on the chemical durability of the glass. A simple and satisfactory explanation of the voltage departure is thus obtained. The authors conclude that the asymmetry potential of the glass electrode results from differences in the ability of the inner and outer surfaces of the electrode to absorb ions. R.A.H.

Electric breakdown of glasses and crystals as a function of temperature. A. VON HIPPEL AND R. J. MAURER. *Phys. Rev.*, **59**, 820–23 (1941).—The effect of order and disorder upon the breakdown characteristics of ionic materials has been investigated. While the dielectric strength of the alkali-halide crystals increases steeply with temperature in the lower temperature range, the trend in glasses is found to be the opposite. A comparison of the characteristics of silica glass with those of quartz confirms the

fact that the positive temperature coefficient of the dielectric strength is produced by the periodic structure of the crystals. The absolute value of the breakdown strength is appreciably increased in the disordered amorphous state. The situation is explained partly by the influence of temperature and structure upon the scattering of electrons. The increase in resistivity of metals with temperature is an analogous phenomenon. J.L.G.

Experiments on the use of mullite blocks. A. A. LITVAKOVSKIĬ. *Stekolnaya Prom.*, **14** [12] 5–10 (1938).—The use of mullite blocks in six large Fourcault tank furnaces showed that the quality of the glass melted is better; the glass no longer contains grog stones. The life of a tank furnace lined with mullite block with an Al_2O_3/SiO_2 ratio of 2.7 is about one year with a batch containing 25% sulfate and with air cooling. M.V.C.

Factors influencing autoclave chemical-durability tests of glass containers. A. HERMAN. *Jour. Amer. Ceram. Soc.*, **24** [10] 323–27 (1941).—4 references.

Glasses for discharge tubes. BRUNO SCHWEIG. *Glass*, **18** [6] 172–73 (1941).—S. discusses the role of the following types of glasses in the manufacture of tubes for luminescent lighting: ordinary clear glass, colored clear glass, opal glass, and luminescent glass. Luminescent glasses are produced by uniting molten glass with the luminescent material, thus producing the following types: (1) uranium glasses; (2) glasses containing simple or compound sulfides of alkali earths, zinc, cadmium, etc.; (3) glasses containing special silicates or tungstates, such as zinc silicate; (4) glasses containing zinc, cadmium, or calcium sulfides with different heavy metals or rare earths. B.C.R.

Glasslike state. O. K. BOTVINKIN. *Izvest. Akad. Nauk S.S.S.R., Ser. Fiz.*, **4**, 600–603 (1940).—Crystals discovered in glasses are not structural elements of them but the products of devitrification. The aggregates of simple or associated molecules composing glass are homogeneous in their chemical composition, the temperatures of complete aggregation being different for each type of grouping. Binding between molecules and aggregates of glass is considerably weaker than that between atoms in a molecule of the silicates. Tetrahedric groups (SiO_4) are connected mainly with the internal structure of the silicate molecules and not with the structure of the aggregates (with the exception of the structure of quartz glass). B.Z.K.

Heat loss in firing a glass furnace. OTTO T. KORITNIG. *Glashütte*, **71** [15] 217–20 (1941).—In estimating the quantity of heat lost, it is important to determine what charge gives the highest thermal efficiency and what relation the strength of the draft or the charge has to the efficiency of the furnace. The quantity of heat fed to the furnace can be accurately fixed, but it is seldom possible to determine by direct measurement the quantity of heat drawn off. Ten ways in which heat is lost may be grouped under losses in the burning of the fuel and losses from heating surfaces: (1) Loss of heat when firing up after the furnace has been idle. The masonry and conduits must be heated up, and the quantity of heat required cannot be calculated. (2) Heat lost because of the incomplete combustion of the fuel gases, which can be calculated from the chemical analysis of the composition of heating gases in relation to the unburned gases. Formulas for computing the quantity of fuel gas to be obtained from 1 kgm. of fuel and the approximate loss through incomplete combustion of the contents of the fuel gas are given. (3) Loss of heat caused by the incomplete burning of ash and cinders, especially with low quality fuels from which slag must be burned out. An average sample of ash can be tested by burning it in a crucible, and the quantity of heat lost can be calculated according to formulas which are explained. (4) Loss of heat brought about when ashes and slag are removed while still hot. By providing a sufficiently large ash chamber, the ash can remain until all of its heat is utilized. (5) Loss of heat from unburned gases which can be determined by testing the waste gases for their CO, CH_4, and heavy hydrocarbon content. Formulas are given. (6) Loss from soot in the waste gases. (7) Loss from radiation from the fire chamber. (8) Loss from waste gases which are warmer than the outside air. (9) Loss from radiation and conduction of heat by the masonry if not tight. (10) Loss from cooling of the generator and furnace. M.V.C.

Increasing the productivity of tank furnaces in work with Aral sulfate. V. A. SHEPTELEVICH. *Stekolnaya Prom.*, **14** [11] 6 (1938).—The tank furnace of the Gobbe system was slightly reconstructed, and the method of feeding the batch was changed. M.V.C.

Influence of chemical treatment on the surface of optical glass. H. SCHRÖDER. *Z. Tech. Physik*, **22** [3] 75 (1941); see *Ceram. Abs.*, **20** [9] 214 (1941). W.M.C.

Measuring the internal area of section of a glass tube. D. J. BEHRENS. *Phil. Mag.*, **31**, 199–203 (1941).—In certain experiments it is desirable to measure the exact internal sectional area of a glass tube at a particular point. An experimental method is described, and formulas are developed which make it possible to measure the area without breaking the tube at the point concerned. R.H.

Mechanical properties of glasses. YA. I. FRENKEL. *Izvest. Akad. Nauk S.S.S.R., Ser. Fiz.*, **4**, 595–99 (1940).—Maxwell's relaxation theory of the elasticity of amorphous bodies (glasses) is briefly examined and illustrated by electrical circuits with a capacity (corresponding to the reciprocal of rigidity) and a resistance (corresponding to viscosity) either in parallel or in series with each other. The former shows schematically a shearing strain, while he latter shows a volume deformation. B.Z.K.

Melting and working of quartz glass. WALTER HÄNLEIN. Translated and condensed in *Glass Ind.*, **22** [8] 345–48 (1941); see *Ceram. Abs.*, **20** [10] 235 (1941). A.P.

Phosphates in ceramic ware: III, Phosphorus compounds as reducing and fining agents in glass. WOLDEMAR A. WEYL AND NORBERT J. KREIDL. *Jour. Amer. Ceram. Soc.*, **24** [10] 337–40 (1941).—6 references, 1 figure. For Part II see *ibid.*, [8] 245–47.

Practical experience in the installation and advantageous use of mullite tank furnaces. YU. TS. VINOGRAĬ. *Stekolnaya Prom.*, **14** [12] 10–15 (1938).—Details of lining tank furnaces of the Konstantinovskiĭ works with mullite blocks are discussed. The glass melted was of much better quality than that melted in grog-lined tanks. The chief characteristic of glass melted in a mullite tank furnace is its uniform quality. In spite of the high cost of mullite blocks, V. recommends their use in glassworks manufacturing safety and plate glass. M.V.C.

Selenium blisters in topaz glass. G. KÖRRN. *Keram. Rundschau*, **47** [7] 66–67 (1939).—Topaz glasses with a strong reddish hue are often difficult to produce in perfect condition because it is necessary to add larger amounts of Se; under these conditions, Se is difficultly soluble and causes the so-called "selenium blisters." These defects can be avoided without causing any change in color by adding 2 kgm. fluorspar to a batch with 100 gm. sand; the glass comes out perfectly pure in the desired color. The application of this method to engobe glasses requires some caution, however, as the expansion coefficients of the body and the engobe must be maintained and the amount of lime must be reduced by an amount equal to the quantity of CaO formed by the reaction of the Ca in CaF_2 with the SiO_2 of the sand. The calculation of this amount is illustrated by an example. M.H.

Sodium fluoride as raw material for glass. A. THÜRMER. *Keram. Rundschau*, **47** [23] 255–56 (1939).—Experiments were made to determine the suitability of sodium fluoride as a decolorizer, either alone or in combination with other substances such as oxidizers, halogen compounds, or other decolorizers. A soda glass of $68SiO_2$, $12CaO$, $20Na_2O$, and an average of 0.08% Fe_2O_3 was used for the test. Results showed that NaF is effective in comparatively small amounts but that an increase to 1.5 to 3.0% does not improve its effect. The presence of $NaNO_3$ increases the decolorizing effect as does the simultaneous presence of NaF and MnO_2 or NaF and $KClO_3$. NaF does not require a change in the Fe content in the glass as do most decolorizers; on the contrary, the decolorizing effect is more intense with a higher Fe content. An absolute

decolorization does not take place; this indicates that no iron fluorides which escape from the melt are formed. A small NaCl addition, which is often recommended for other decolorizers, does not enhance the effect of NaF, but the presence of suitable oxidizers and a trace of Se gives a complete purity of color. 15 references. M.H.

Spectrochemical analysis of glass sand. MORRIS SLAVIN. *Glass Ind.*, **22** [8] 341–43 (1941).—Spectrographic technique is applicable to routine glass-plant control as well as to research problems. The method is briefly described. 15 references. A.P.

Structure of glasses according to X-ray analysis and optical properties. A. A. LEBEDEV. *Izvest. Akad. Nauk S.S.S.R., Ser. Fiz.*, **4**, 584–87 (1940).—Na silicate glasses were investigated by means of X rays and residual changes in the index of refraction upon heating in order to determine the structure. Results show the presence of at least two crystalline modifications of silica, viz., cristobalite and tridymite. X rays show in addition that crystallites of Na metasilicate may also be present. B.Z.K.

Structure and properties of glasses from the point of view of the phase rule. K. G. KUMANIN. *Izvest. Akad. Nauk S.S.S.R., Ser. Fiz.*, **4**, 588–94 (1940).—The internal structure of glass is composed of cybotactical groups whose structure is a singular reflection of the structure of the first crystal phase of the given composition. Accurate investigations of the manifold properties of glasses show the course of their change on the boundaries of the phase fields. Within the limits of one system or another a stable glasslike state is connected with the phase boundaries of the fields and triple points where, during crystallization, competition takes place between the various crystal phases, often for one kind of molecule. From the viewpoint of the phase rule, glass is the product of a nonequilibrium cooling of a melted solution. B.Z.K.

Structure of solid glasses according to data of electrical conductivity. R. L. MÜLLER. *Izvest. Akad. Nauk S.S.S.R., Ser. Fiz.*, **4**, 607–15 (1940).—M. proposes a theory for the electrolytic dissociation in refractory inorganic glasses. According to this theory, the metallic cations are distributed in equilibrium in a thermodynamically nonequilibrium glasslike system. The cations are situated near the ionized or nonionized oxygen atoms. The theory is based on the experimental data on the electrical conductivity of alkaline boron and silicate glasses. B.Z.K.

Studies of the chemical durability of glass by an interferometer method. DONALD HUBBARD AND EDGAR H. HAMILTON. *Jour. Research Nat. Bur. Standards*, **27** [2] 143–57 (1941); RP 1409. Price 5¢.—An interferometer method for determining the chemical durability of glass has been tried on a series of typical glasses over a wide range of temperature and pH. The results show the importance of careful temperature control if comparisons are to be made between the findings of different investigators. The relations between amount of attack and pH for some of the glasses show pronounced inflections near pH 7 in the presence of Britton universal buffer, while the attack by distilled water for these same glasses is very slight in comparison. The results also strongly emphasize the fact that there can be no single test by which the durability of glass can be judged with respect to all conditions of service. The method has proved particularly useful in the interpretation of known voltage anomalies of the glass electrode. R.A.H.

Tests for the chemical durability of bottles. A. J. LIEBMANN AND M. ROSENBLATT. *Jour. Amer. Ceram. Soc.*, **24** [10] 328–37 (1941).—17 references, 4 figures.

Thin glass for microscope cover slips. ANON. *Glass*, **18** [6] 174 (1941).—The year 1940 marked the centenary in England of the manufacture of thin glass cover slips. Prior to 1840 it was necessary to use thin talc or mica for this purpose. The principal change in the constitution of the glass during this period was made in 1928 when a glass was introduced which was capable of withstanding sterilization and exposure to tropical atmospheres without deteriorating i.e., clouding. B.C.R.

PATENTS

Apparatus for making multicellular glass. S. L. WILLIS (Corning Glass Works). U. S. 2,255,237, Sept. 9, 1941 (Nov. 5, 1937; June 7, 1938).

Apparatus for producing mineral wool. J. R. PARSONS (U. S. Gypsum Co.). U. S. 2,255,227, Sept. 9, 1941 (Nov. 10, 1938).

Bottle-buffing machine. A. J. WEISS (Maryland Glass Corp.). U. S. 2,254,671, Sept. 2, 1941 (Feb. 6, 1939).

Die for molding or casting optical lenses. PAUL GENESY (Jenkel-Davidson Optical Co.). U. S. 2,253,697, Aug. 26, 1941 (July 11, 1938).—A die for casting or molding optical lenses comprises a sillimanite base and a layer of glass fused to one side of the base, the layer of glass being formed with an optical surface.

Electric furnace. C. A. BAKER (Owens-Corning Fiberglas Corp.). U. S. 2,255,578, Sept. 9, 1941 (Sept. 9, 1937).—An electric furnace for processing high melting point materials.

Glass composition. R. H. DALTON (Corning Glass Works). U. S. 2,255,558, Sept. 9, 1941 (April 22, 1939).—A glass consisting of silica (91 to 95%), boric oxide, and alumina (4 to 8%).

Glass composition and products thereof. E. D. TILLYER, H. R. MOULTON, AND T. M. GUNN (American Optical Co.). U. S. 2,254,633, Sept. 2, 1941 (May 26, 1939).—A vitreous composition whose analysis is zinc oxide 40 to 60 and boric anhydride 40 to 60% and a stabilizer introducing 0.5 to 2.5% beryllium, based on the batch.

Glass flatness measuring device. C. M. TUTTLE AND R. V. CARTWRIGHT (Canadian Kodak Co., Ltd.). Can. 398,411, Aug. 5, 1941 (March 8, 1940; in U. S. Sept. 13, 1939). G.M.H.

Glass sheet tempering apparatus. WILLIAM OWEN (Pilkington Bros., Ltd.). Can. 398,620, Aug. 12, 1941 (Oct. 2, 1939; in U. S. Oct. 14, 1938). G.M.H.

Glass-tempering method and apparatus. E. J. LEWIS (Corning Glass Works). U. S. 2,254,227, Sept. 2, 1941 (April 22, 1937).

Ink for glass. J. C. WILSON (Westinghouse Electric & Mfg. Co.). U. S. 2,254,865, Sept. 2, 1941 (Oct. 31, 1939).—An ink comprising about 20.9% pigment by weight, about 4.2% mineral filler by weight, about 1.2% argentic oxide by weight, and about 73.7% glycerine by weight.

Interior frosted glass article. H. S. WILLSON (Corning Glass Works). Can. 398,722, Aug. 19, 1941 (March 7, 1939; in U. S. April 26, 1938). G.M.H.

Luminescent glass and electric discharge lamp made therefrom. HELLMUTH FISCHER. U. S. 2,255,109, Sept. 9, 1941 (Sept. 26, 1939).—Luminescent glass of the uranium-lead type carrying a luminescence-affording content of a compound of a metal of the group that consists of uranium and lead, the glass being of intensified luminescence by virtue of an alkali content in which potassium oxide is preponderant over sodium oxide by at least a 2:1 ratio and a zinc oxide content of substantially 3.5 to 7.0%.

Machine and method for forming hollow glassware. E. G. BRIDGES (Lynch Corp.). U. S. 2,254,992, Sept. 2, 1941 (Nov. 30, 1937).

Making multicellular glass. S. L. WILLIS (Corning Glass Works). U. S. 2,255,238, Sept. 9, 1941 (Nov. 25, 1939).

Method and apparatus for forming and refining glass. K. B. MCALPINE (Pittsburgh Plate Glass Co.). U. S. 2,254,079, Aug. 26, 1941 (Feb. 6, 1940).

Molded fluorescent lamp. J. W. MARDEN AND GEORGE MEISTER (Westinghouse Electric & Mfg. Co.). U. S. 2,255,431, Sept. 9, 1941 (Oct. 21, 1939).

Multicellular glass. S. L. WILLIS (Corning Glass Works). U. S. 2,255,236, Sept. 9, 1941 (Nov. 5, 1937).—Glass which contains a multiplicity of small bubbles of gas under positive pressure at room temperature.

Multifocal lens and method of making. H. R. MOULTON (American Optical Co.). U. S. 2,254,440, Sept. 2, 1941 (Aug. 18, 1939).

Polish meter. M. L. DEVOL (Pittsburgh Plate Glass Co.). U. S. 2,254,062, Aug. 26, 1941 (March 31, 1938).—Apparatus for determining the polish of a glass plate.

Process and apparatus for the manufacture of hollow building units. WILLIAM OWEN (Pittsburgh Plate Glass Co.). U. S. 2,254,086, Aug. 26, 1941 (Nov. 13, 1937).

Silvering of mirrors. PEACOCK LABORATORIES, INC. Brit. 537,987, July 30, 1941 (Oct. 27, 1939). Brit. 538,026, July 30, 1941 (Nov. 16, 1939).

Structural Clay Products

Construction of Queens Midtown Tunnel. DAVID G. BAILLIE, JR. Presented at meeting of National Paving Brick Assn., Toledo, Ohio, Jan., 1941; *Dependable Highways*, No. 170, pp. 6–7, 10–12 (1941).—Construction details of the tunnel and the paving-brick roadway are given. Illustrated. P.S.D.

Discussion of Queens Midtown Tunnel. W. L. BARR. Presented at meeting of National Paving Brick Assn., Toledo, Ohio, Jan., 1941; *Dependable Highways*, No. 170, pp. 12–14 (1941). P.S.D.

Modern brick manufacture. ANON. *Gas World [Ind. Gas Supp.]*; reprinted in *Claycraft*, **14** [8] 212 (1941).—A method of heating the dies on a brick machine by special gas burners, allowing for a faster flow of clay through the dies, is described. Both upper and lower dies are constructed in the form of small ovens and heated by special gas burners. Chrome steel is used, as it remains rigid at high temperatures. Since heating causes the dies to expand, both upper and lower dies must receive the same heat. A burner was designed to ensure complete combustion of the gas within the small space of the dies, and high-pressure gas is used. G.A.K.

Standardization of brick. ANON. *Claycraft*, **14** [10] 241 (1941).—Standardization of common brick to two sizes has been agreed upon by manufacturers throughout England and Wales. Standard specifications are as follows: length tolerance $8^1/_4 \pm {}^1/_8$ in., width tolerance $4^1/_{16} \pm {}^1/_{16}$ in., and depth tolerance (Type II) $2^5/_8 \pm {}^1/_{16}$ in. and (Type III) $2^7/_8 \pm {}^1/_{16}$ in. G.A.K.

Thermal expansion of clay building brick. CULBERTSON W. ROSS. *Jour. Research Nat. Bur. Standards*, **27** [2] 197–216 (1941); RP 1414. Price 10¢.—The coefficients of thermal expansion of 139 brick were measured over the range −10° to +40°C. These brick included 1 sample of sand-lime, 9 of fire-clay, and 61 of clay and shale brick. The clay and shale brick represented a wide range in properties and included samples from various districts in the United States. The coefficients of 87% of the clay and shale brick were between 5 and 7 millionths per °C. The average coefficient of the clay brick was 6.0, of the shale brick 6.1, and of the fire-clay brick 3.9 millionths per °C. No relation was observed between the thermal expansion and the other physical properties of the brick. R.A.H.

BOOK

Handbook of Testing Materials: Vol. III, Testing Nonmetallic Building Materials (Handbuch der Werkstoffprüfung: III Band, Die Prüfung der nichtmetallischen Baustoffe). OTTO GRAF, editor of vol. III. Julius Springer, Berlin, 1941. 800 pp., 497 illustrations. Price Rm. 75; bound, Rm. 78. Reviewed in *Ber. Deut. Keram. Ges.*, **22** [5] 202 (1941).—The ceramist will be interested especially in the section by H. Hecht on the testing of brick (pp. 224–325) and that by F. Weise on the testing of brick masonry (pp. 325–30). Other sections on the testing of mortar, cement, and glass should be of value. W.H.H.

Refractories

Basic-brick roof construction. H. S. ROBERTSON. *Proc. Open-Hearth Conference, Amer. Inst. Mining & Met. Engrs.*, **1940**, pp. 44–50.—A change in roof construction is necessary if basic brick are to be substituted for silica brick owing to their lower strength and higher expansion and contraction. A full suspended roof of basic brick is used for copper reverberatory furnaces, 100 x 28 ft. in size. Each brick is encased in metal and suspended individually. These have lasted over a year, four to five times longer than silica brick. Open-hearth roofs in Europe, with a life exceeding 1000 heats, use a different construction. An arch is held to a definite shape, to distribute the strain more evenly, by suspending the skewback channel. Other changes are necessary; it must be possible to clear the slag pockets and checkers during operation. At least 50% of the economy is from the continuous operation, while the remainder is time saved with higher operating temperatures. There are suitable refractories available in this country. W.D.F.

Economical manufacture of tank blocks. JOSEF GREWE. *Keram. Rundschau*, **47** [11] 115–16; [12] 127–29; [13] 139–40 (1939).—G. discusses the economical manufacture of tank blocks (from the German viewpoint) and describes the manufacturing processes, shapes, and equipment. The most suitable material is a clay which can be fired dense at temperatures which are not too low. Clays which sinter early become too soft at higher temperatures and will therefore deform in the manufacturing process. M.H.

Field for special refractories in the open hearth. LOUIS A. SMITH. Presented at meeting of Refractories Division, American Ceramic Society, Conneaut Lake, Pa., Sept., 1939; abstracted in *Brick & Clay Record*, **95** [4] 55–56 (1939).—The substitution of plastic chrome for part of the magnesite in laying a basic open-hearth bottom produces a safer bottom at less cost. In the front walls, above the slag line, silica brick have given about as good service as other types, although chrome-magnesite brick, either fired or unfired, laid with metal joints, are the most likely to show improvement over silica. Neither mullite nor superduty brick showed to advantage in the roof or front, back, or end walls. Superduty brick have been used to advantage in patching small holes in the roof, providing the patch is not required to remain more than 7 to 10 days. B.C.R.

Heating-furnace refractories: II. EVERETT C. HITE AND GILBERT SOLER. *Brick & Clay Record*, **96** [6] 51–52, 62 (1940).—Heating, annealing, and normalizing furnaces are usually built of similar materials, although the design may vary considerably. The working face of these furnaces is usually constructed with some type of insulating material. The furnaces may be designed for direct, muffle, or radiant tube firing, using such fuels as natural gas, fuel oil, electricity, or various manufactured low B.t.u. gases. Vitrification of roof brick, resulting in possible dripping, may occur with the direct-firing type of furnace. In either the muffle or the radiant-tube type of furnace, flame impingement is not usually a serious factor, as the muffle is made of a dense refractory or may even be made of metal, and in the radiant-tube furnace the flames are inclosed in the tubes. With the use of carbonaceous gases for maintaining a nonoxidizing atmosphere, disintegration of the refractories may occur. In forging furnaces, the desirable properties of the refractories are high mechanical strength, resistance to spalling, high softening point under load, and a high fusion point. Although plastic chrome ramming mixes and superduty firebrick are usually used, furnace hearths made of limestone, which must be rebuilt after several days' run, have been used. For Part I see *Ceram. Abs.*, **20** [10] 238 (1941). B.C.R.

Increase of the solubility of alumina contained in kaolin due to preheating in different gases. G. F. HÜTTIG AND E. HERRMANN. *Z. Elektrochem.*, **47** [3] 282–86 (1941); see *Ceram. Abs.*, **20** [7] 170 (1941). J.M.N.

Interreaction of silica with slate, slate coke, and ashes at higher temperatures. V. A. BRON. *Ogneupory*, **9** [2] 85–90 (1941).—Slate, slate coke, and ashes react with silica

more intensively than coal coke and slag. The effect of slate coke is especially powerful; silica is destroyed at 1300°. B. recommends the use of dense silica bodies. Grog and semiacid refractories are more resistant to the action of slate coke than silica. M.V.C.

Magnesium oxide from dolomite and its use in the manufacture of highly refractory products. P. P. BUDNIKOV AND I. I. RIVLIN. *Trudy Kharkov. Khim.-Tekh. Inst.*, **3**, 154–62 (1941).—Several French patents dealing with the separation of magnesium oxide from dolomite fired at 900° were tested. The optimum temperature for firing dolomite and the temperature of its treatment with ammonium chloride were determined. Samples of refractory forsterite material were obtained from a mixture of concentrated dolomite and serpentinite. Petrographic study showed that the samples contained small grains of forsterite and periclase. M.V.C.

Manufacturing graphite stoppers and ladles at the Luch Svobody Plant. V. K. KAMINSKIĬ AND P. N. YUNAK. *Ogneupory*, **9** [2] 77–84 (1941).—The technological process of manufacturing graphite stoppers and ladles and experiments with them in open-hearth furnaces are described. These products were found satisfactory. M.V.C.

New development in basic refractory masses. C. R. PLATZMANN. *Sprechsaal*, **73**, 218–22 (1940); abstracted in *Chem. Zentr.*, **1940, II**, 1766.—Publications on the subject are reviewed. M.V.C.

Particle sizing and ball-mill grinding aids machine pressing of silica shapes. ANON. *Brick & Clay Record*, **93** [6] 26, 28, 30 (1938).—Through careful control of the particle sizing of ganister, refractory shapes previously made only by hand may now be power-pressed. Fines necessary to produce the desired screen analysis are obtained by ball milling; an air separator is used for removing the coarse particles. A flow sheet is given. B.C.R.

Principal physical tests for fire-clay refractories: III. R. S. BRADLEY. *Brick & Clay Record*, **96** [6] 53–54, 56 (1940).—B. describes the panel spalling test, in which a panel of brick, after being reheated to 1600° or 1650°C., is alternately heated to 1400°C. and cooled with an air-water mist. **IV.** *Ibid.*, **97** [1] 47–48 (1940).—B. describes the construction and operation of a standard load test furnace for subjecting refractories to a definite load at elevated temperatures, usually 1350° and 1450°C. Both the lever and direct types of applying the load are shown drawn to scale. For Parts I and II see *Ceram. Abs.*, **20** [10] 239 (1941). B.C.R.

Pyrometric cone equivalent determinations. EARL C. PETRIE. *Bull. Amer. Ceram. Soc.*, **20** [9] 299–302 (1941). —8 figures.

Refractories—constitution and reactions. J. F. HYSLOP. *Jour. West Scot. Iron & Steel Inst.*, **48** [3] 39 (1940–41).—H. discusses briefly the constitution of the mineral oxides and the replacement of metal ions. As the more basic oxides tend to displace those less basic, the addition of lime to magnesium silicate displaces the magnesium-forming calcium silicate and periclase. In chrome or chrome-magnesia refractories, the silicates of the chrome ore tend to take up some R ions on heating and form low-melting compounds having the general composition $MgO \cdot R_2O_3 \cdot SiO_2$. These compounds give the refractory a low load-bearing property and low resistance to thermal spalling. In reaction tests in which 60-mesh powders were spread on chrome brick and heated at 1600°C. for 1 hr., pure alumina absorbed Fe_2O_3, Cr_2O_3, and MgO from the brick; magnesite absorbed Fe_2O_3 and Cr_2O_3 when heated in a similar manner; and Mg aluminate absorbed Fe_2O_3 and Cr_2O_3. The data supported the contention that, under oxidizing conditions, chrome ore releases Fe^{+++} and that it tends to break up ionically at high temperatures. In a similar test, diopside ($CaO \cdot MgO \cdot 2SiO_2$) reacted with a chrome-magnesite brick, leaving only red-brown periclase crystals having an analysis of SiO_2 8.4, Cr_2O_3 2.3, Al_2O_3 2.0, Fe_2O_3 2.7, MgO 83.6, and CaO 0.9%. In an X-ray examination of a chrome-magnesite brick attacked by mill scale, magnetite and a little Mg ferrite were present in the uppermost zone; beneath this zone the amount of Mg ferrite increased, after which only chrome crystals appeared. A magnesium aluminate brick which burst, through attack by scale, showed the following zones: (1) Fe_3O_4 (contracted lattice); (2) Mg aluminate (expanded lattice), Mg ferrite, Fe_3O_4 (smal amount); (3) Mg aluminate (slightly expanded lattice); (4) Mg aluminate (normal). In a forsterite brick which was attacked by scale but did not burst, the following zones appeared: (1) Mg ferrite and Fe_3O_4; (2) forsterite and a small amount of fayalite and Mg ferrite; (3) forsterite. B.C.R.

Special ceramic masses for technical purposes. T. H. TIVES. *Keram. Rundschau*, **47** [26] 289–91; [27] 302–304 (1939).—The three most important aluminosilicates are sillimanite, andalusite, and disthene (kyanite). Disthene is a transition product of sillimanite and andalusite which is formed on heating to about 1300°C.; at higher temperatures, mullite is formed. Andalusite and sillimanite have the composition 37.05 SiO_2 and 62.95% Al_2O_3; they are not disintegrated by acids and are dissolved only by alkali carbonate and soluble caustic alkali; the melting point is 1816°C.; sillimanite softens at 1545°C. Mullite is a compound consisting of $3Al_2O_3 \cdot 2SiO_2$; it is formed at high temperatures from sillimanite, andalusite, kyanite, and dumortierite during liberation of SiO_2 as SiO_2 glass. By adding more Al_2O_3, the vitrification is reduced and the mullite formation is increased. Complete mullite formation appears at $3Al_2O_3 \cdot 2SiO_2$ (71.8% Al_2O_3 and 28.2% SiO_2). The softening point is 1810°. A mullite-rich fire clay is produced by firing clay to softening (Sinton fire clay). Mullite is not dissolved by hydrofluoric acid. For the formation of mullite, certain substances ("crystallizers") must be present in the raw material, e.g., finely ground corundum, V-containing minerals, or Ti-containing minerals such as rutile, anatase, or brookite. High-grade porcelain, especially for high-tension purposes, must have a heterogeneous structure of a vitreous mass of K_2O, Na_2O (CaO-FeO), Al_2O_3, SiO_2, and sillimanite-mullite solid solutions. Quartz (SiO_2) materials are formed by the electric melting of quartz; corundum (Al_2O_3) is formed by the electric melting of alumina or alumina-rich minerals. A less known Al_2O_3-containing raw material is pyrophyllite (also called agalmatolite), a H_2O-containing aluminosilicate with greatly varying Fe and alkali contents. The compositions of various important deposits of Al_2O_3 minerals are given. BeO, having a melting point of 2500°C., is superior to Al_2O_3; it is chemically very stable and is not attacked by reducing agents. It has a high heat conductivity and therefore an excellent resistance to temperature changes, the highest resistance of all ceramic substances. Dielectric losses are very low. The most important mineral for its production is beryl, $3BeO \cdot Al_2O_3 \cdot 6SiO_2$. It reacts very strongly at high temperatures with other oxides. Periclase (MgO) is formed by the electric melting of magnesite; the melting point is 2800°C. Magnesite brick of molten magnesia will stand a pressure of 2 kgm. per cm.^{2} at 2000°C. without softening. MgO is volatile over about 2000°C. in a reducing atmosphere and does not combine with C. Its expansion coefficient is 13×10^{-6} (20° to 600°), and it is therefore extremely sensitive to temperature changes. At high temperatures (800° to 1200°C.) MgO has a better electric insulating capacity than kaolin, sillimanite, and silica brick. MgO + 5% Al_2O_3 softens at 1242°, and MgO + 5% SiO_2 at 1398°. For electric high-frequency purposes, forsterite is an important material. It is formed by MgO accumulation with magnesite, brucite, or nemalite up to 70% and talc or soapstone. Its composition is $2MgO \cdot SiO_2$ (57.3% MgO and 42.7% SiO_2), and the melting point is 1890°. Clinoenstatite is a normal silicate or a metasilicate, $MgO \cdot SiO_2$, monoclinic (40% MgO and 60% SiO_2); it disintegrates into forsterite at 1575°. Cordierite, $2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$ (13.7 MgO, 35 Al_2O_3, and 51.3% SiO_2), has an expansion coefficient of 1×10^{-6}. Cordierite mixtures should not be fired higher than Seger cone 14 because at higher temperatures (1450°) dissociation begins. In this system a eutectic exists which melts at 1345°; it has the formula $MgO \cdot 0.356Al_2O_3 \cdot 2.03SiO_2$. Soapstone and talc both have the composition $3MgO \cdot 4SiO_2 \cdot H_2O$ (31.75

MgO, 63.45 SiO_2, and 4.8% H_2O); soapstone has a finely crystalline, almost amorphous structure, while talc has a coarsely crystalline leafy structure and is nonplastic in the finely ground state. Dehydration takes place between 850° and 960°C. when a molecular disintegration into clinoenstatite and cristobalite (β-modification) occurs. Chlorites or chlorite slates are micalike materials of 26 SiO_2, 20 Al_2O_3, 42 MgO + FeO, and 12% H_2O; to this group belong the minerals penninite, leuchtenbergite, kämmererite, clinochlore, ripidolite, pygnotrop, delessite, thuringite, etc. They differ from mica in their high water content and lack of CaO and from talc in their Al_2O_3 content. They are fireproof and are used for stove plates and pots because of their good cutability. Steatite masses consist mainly of soapstone with small additions of fluxes and clay for plasticization. The Seger formulas for three typical steatite masses are as follows:

0.970 MgO 0.001 K_2O 0.014 CaO 0.015 FeO	0.076 Al_2O_3	1.428 SiO_2
0.9726 MgO 0.0132 CaO 0.0139 FeO	0.2667 Al_2O_3	1 2519 SiO_2
0.9049 MgO 0.9017 K_2O 0.0005 CaO 0.0029 FeO	0.057 Al_2O_3	1.38 SiO_2

These masses were fired to Seger cones 13, 13, and 14, respectively. TiO_2 is also used for high-frequency purposes; its dielectric constant is 80. It is trimorphous and occurs naturally in two tetragonal forms, anatase and rutile, and in rhombic form as brookite. Artificially produced TiO_2 transforms above 1390°, into rutile which is the most stable of all titanium oxides at all temperatures and pressures. Natural rutile melts at 1560°, and pure TiO_2 at 1825°. TiO_2 resists all acids except concentrated H_2SO_4. TiO_2 acts as a flux in kaolins and clays; the addition of 10% TiO_2 lowers the melting point of pure kaolin 100°C. ZrO_2 has a melting point of 3000°, an expansion coefficient of 8.4×10^{-7}, a comparatively low thermal conductivity, a high resistance to temperature changes, and a high resistance to strongly acid and basic agents. Pure ZrO_2 is perfectly nonplastic and is difficult to mold. At high temperatures, its electric conductivity is so high that it acts as heating resistance in the electric arc and as a conductor in the melt. Natural zirconium silicate disintegrates at high temperatures; SiO_2 becomes volatile, and ZrO_2 remains. The body does not become entirely dense, and it is well suited to sudden temperature changes; it is more resistant to acid than to basic substances. It should not be used above 1750°C. Zirconium orthosilicate ($ZrO_2 \cdot SiO_2$) contains 67.2% ZrO_2 and 32.8% SiO_2, with some Fe as impurity. It is used in metallurgical processes because of its resistance to strongly alkaline melts; it is, however, sensitive to iron silicate slags at high temperatures. M.H.

Thermoinsulation of open-hearth furnaces. Yu. Yu. Gapanovich. *Ogneupory*, 9 [2] 101–104 (1941).—The use of diatomite for the thermal insulation of open-hearth furnaces is discussed. M.V.C.

Where refractories are used by six major industries. Anon. *Brick & Clay Record*, 95 [4] 58–60, 62 (1939).—Tables showing the types of refractories used in various parts of the construction and the conditions existing at those points are given for the following industries: by-product coke oven, open hearth, malleable iron, lead, copper, and glass industries. These tables were taken from "Manual of A.S.T.M. Standards on Refractory Materials, 1940–1941" (*Ceram. Abs.*, 20 [5] 119 (1941)). B.C.R.

PATENTS

Bauxite impregnation. Blakeslee Barnes (Chemical Construction Corp.). Can. 398,585, Aug. 12, 1941 (Aug. 25, 1938; in U. S. Sept. 22, 1937).—A method of impregnating bauxite with carbon comprises heating calcined bauxite and acid sludge above the decomposition point of the latter, whereby SO_2 is evolved and carbon is formed within the bauxite pores, and burning out a portion of the carbon so formed. G.M.H.

Chrome refractory brick and method of manufacture. R. P. Heuer (General Refractories Co.). U. S. 2,253,620, Aug. 26, 1941 (Nov. 5, 1938).—(1) A method of manufacturing refractory brick composed principally of chrome ore and suitable for use in a furnace without kiln firing comprises grinding the chrome ore to pass a screen having 5 mesh per linear in., mixing it with water, sulfuric acid in amount between 0.5 and 2%, kaolin in amount between 1 and 5%, bentonite in amount between 0.1 and 3%, and more than 15% of magnesia, pressing the mixture into brick under pressure exceeding 1000 lb. per sq. in., heating the brick for at least 12 hr. at a temperature between 125°F. and the boiling point of water in an atmosphere substantially saturated with moisture before the excess content of moisture is removed, and subsequently continuing the heating to remove the excess moisture content. (10) A refractory brick composed principally of chrome ore and suitable for use in a furnace without kiln firing comprises chrome ore of 5 mesh per linear in., sulfuric acid in an amount between 0.5 and 2%, kaolin in amount between 1 and 5%, bentonite in amount between 0.1 and 3%, and more than 15% of dead-burned magnesite, the brick having a crushing strength at room temperature in excess of 5000 lb. per sq. in. and an apparent specific gravity at room temperature in excess of 3.04.

Furnace wall. J. J. Offutt (A. P. Green Fire Brick Co.). U. S. 2,255,803, Sept. 16, 1941 (Jan. 2, 1941).

Magnesia-coated refractory particles and their preparation. G. A. Hebbe and R. E. Gibbs (J. E. Baker Co.). U. S. 2,253,955, Aug. 26, 1941 (July 14, 1938).—A process of preparing coated refractory particles comprises heating and agitating fired dolomitic particles mixed with a minor proportion of a finely divided relatively pure magnesium compound and a bonding agent therefor to ceramically bond magnesia to the surfaces of the dolomitic particles and thereby increase the magnesia content of the surfaces of the particles.

Making refractory bodies of tin oxide. Dan McLachlan, Jr. (Corning Glass Works). U. S. 2,256,033, Sept. 16, 1941 (May 18, 1940).—A method of making a refractory body comprises molding a batch containing a substantial amount of stannic oxide, firing the molded body at a temperature and for a time sufficient to sinter it to a coherent porous mass, impregnating the porous body with a solution containing a salt of a metal which when raised to sintering temperatures will accelerate the shrinkage of the refractory, the amount of metal introduced into the body being equivalent, as oxide, to 0.5 to 2% of the weight of the body, drying the impregnated body, and firing it in an oxidizing atmosphere at 1300° to 1500°C.

Terra Cotta

Colors of ceramic tile. Parry Moon. *Jour. Optical Soc. Amer.*, 31, 482–87 (1941).—Spectrophotometric reflection curves were obtained on 91 samples of tile from three American tile manufacturers. Fourteen reflection factor vs. wave length curves summarize the results of various color groupings. A table gives data on manufacturers' specifications, approximate color, and calculated trichromatic coefficient (x and y) and reflection factor for both illuminant A (incandescent lamp) and illuminant C (daylight). The values of reflection factor allow the calculation of illumination in rooms having tiled floors or walls and predetermination of the visual effect of changing from one kind of tile to another. As ceramic tile is permanent and carefully controlled for uniformity,

the table permits the use of tile samples as rough comparison standards for judging the color, reflection factor, and Munsell notation of other materials. A.P.

Farm stoves. FRITZ BLÜMEL. *Keram. Rundschau*, **47** [12] 125–27; [14] 150–52 (1939).—B. discusses the historical development of stoves and furnaces in the peasant homes and farmhouses of Germany and describes the artistic features, especially since the invention of tile in the 9th century. Illustrated. M.H.

Installation for the manufacture of tile. ANON. *Keram. Rundschau*, **47** [2] 13–14 (1939).—Installations for preparing and mixing the ingredients are described. Two compositions for gray plates are given.

I

White mass	(kgm.)	Color mill addition	(kgm.)
White-firing clay	2500	Feldspar	150
Lix viated kaolin	1000	Quartz	200
Quartz	1000	Chrome ore	100
Feldspar	500	White-firing clay (fat)	40
		Magnesite	10
	5000		—
			500

II

	(kgm.)		(kgm.)
White-firing clay	2500	Feldspar	350
Lixiviated kaolin	700	Chrome ore	100
Fat, white-firing clay	300	White-firing clay (fat)	50
Feldspar	1500		—
			500
	5000		

M.H.

Tile as ornamental wall decoration in North-German kitchens. FRITZ BLÜMEL. *Keram. Rundschau*, **47** [1] 5–7 (1939).—The extensive use of tile in German, especially North-German, houses in fireplaces and kitchens since the 17th century is described and illustrated by artistic examples. The custom has been revived again to a certain extent. M.H.

PATENTS

Ceramic conduit. CHARLES H. MILLER AND SAMUEL O. MCFALL. Can. 397,545, July 1, 1941 (Nov. 15, 1939). G.M.H.

Tile. N. E. PHILLIPS (Olean Tile Co.). U. S. 2,255,712. Sept. 9, 1941 (July 18, 1940).

Whiteware

All-American sanitary-ware body. I. E. SPROAT, C. C. TREISCHEL, AND E. W. EMRICH. *Jour. Amer. Ceram. Soc.*, **24** [10] 311–17 (1941).—2 references, 6 figures.

Better insulators at lower cost with new mechanized processes. E. H. FISCHER. *Ceram. Ind.*, **37** [1] 52, 54 (1941).—Westinghouse high-tension porcelain insulators are mechanically glazed on glazing machines; the glaze is applied by flooding the rotating unfired insulator with glaze slip. The insulators are dried by radiant heat from infrared reflector lamps. Radio-interference glaze is applied by mechanical dipping. Illustrated. H.T.

Casting. GIRARD W. PHELPS. *Bull. Amer. Ceram. Soc.*, **20** [9] 313–15 (1941).—4 references.

Ceramic parts of accurate size made in automatic presses. GEORGE ADERHOLD. *Ceram. Ind.*, **37** [1] 39 (1941).—Modern automatic presses produce up to 600 small pieces a minute. The ceramic material, consisting chiefly of talc with a minimum addition of abrasive material, has a moisture content of 2% or less. Due to high pressure and low total shrinkage, pieces produced on automatic presses are very accurate and free from warpage. H.T.

Eliminate filter press in preparing sanitary-ware casting slip. ANON. *Ceram. Ind.*, **37** [1] 46–47 (1941).—At the Mansfield Sanitary Pottery, Inc., Perrysville, Ohio, filter presses are entirely eliminated in the preparation of the casting slip by careful control of casting rate, specific gravity, viscosity, and soluble alkali content. The ware is fired in two 130-ft. tunnel kilns directly in open flame, with natural gas as fuel. Illustrated. H.T.

Fritted glazes safe in respect to lead poisoning. HERMANN HARKORT. *Keram. Rundschau*, **47** [3] 21–24; [5] 42–45; [6] 52–55 (1939).—The numerous investigations on the lead solubility of frits have shown unmistakably that the danger of lead poisoning to the workmen doing the glazing cannot fully be eliminated by fritting alone. Additions of boric acid and alkalis reduce the resistance of the lead aluminosilicates to weak acid, i.e., their lead insolubility is reduced to such extent that the effect of fritting is more or less nullified. With a boric acid content of 10% or more, a destructive effect is produced on frits with more than 50% PbO, and the favorable effect of Al_2O_3 in the lead silicates is counteracted by the presence of boric acid. Leadproof glazes can be obtained only by using two frits, one carrying the total PbO content in the form of a leadproof aluminosilicate and the other containing the boric acid in the form of a lead-free borosilicate. In general, the lead-containing frit should have a composition of the type 65 PbO, 33 SiO_2, and 2% Al_2O_3 which melts at 620° to 640°C. A composition of 61.4 PbO, 31.5 SiO_2, and 7.1% Al_2O_3 is better, but its melting point is 100° higher (730°). The effects of additions of other oxides are as follows: K_2O increases lead solubility slightly; ZnO, BaO, and CaO increase it in increasing degree; MgO has no effect or increases it slightly; and CaO decreases it. The lead-free frit must not be disintegrated by water during grinding, as this would change the composition of the glaze. The mill addition must be of such nature that it will take out of the other frits as little as possible SiO_2 and Al_2O_3 and must therefore contain no Na_2O, feldspar, or $CaCO_3$. It should consist only of kaolin or clay and should be added only in such amount as to give good consistency of the glazing paste. H. gives a number of examples showing how the three frits can be made up under varying conditions. The standardization of frits is advocated, and diagrams are developed from which the different constituents can be selected. By using standard frits for colored glazes, a greater safety can be obtained, trial tests can be made inexpensively on a small scale, and the manufacture of glazes and frits is simplified. M.H.

Industrial liquefaction of kaolin and porcelain masses. ANON. *Keram. Rundschau*, **47** [27] 299–300 (1939).—Directions are given for determining the most effective amount of water to be added to kaolin to produce good pouring qualities. On this, the production of ware free from defects often depends. Samples with different contents of soda, water glass, and water were made, and their viscosity, which is an indication of proper liquefaction, was measured. The causes of defects and their prevention are briefly discussed. M.H.

Influence of firing and cooling rates on properties of a vitreous china body. A. E. CURRIER AND A. S. WATTS. *Bull. Amer. Ceram. Soc.*, **20** [9] 307–309 (1941).

Manufacture of vitreous china sanitary ware. JOHANNES WOLLINGER. *Keram. Rundschau*, **47** [52] 549 (1939).—The manufacture of vitreous china requires good kaolins and fat early sintering clays that have as light a color as possible when fired. Only feldspar that gives an opaque, pure white, blister-free glass and has a low melting point should be used. Ca-rich feldspars are unsuitable. Pegmatite and quartz must be free of Fe. A general composition of about 45 clay, 30 quartz, and 25% feldspar will give a satisfactory body at 1200° to 1300°C. Water should be added in such amount that the mass (after preparation) will have a density of 65° Bé; the mass must not leave a residue on a 1000-mesh sieve. By using soda, water glass, and only a little water, plasticity and strength can be exactly controlled. The cast ware must first be dried at 25° to 30°C., if possible under slight air circulation. The ware should be placed on refractory supports

(fire-clay and corundum mixture). A good glaze (pure white) fired at Seger cone 6 is as follows:

$$\left.\begin{matrix}0.30\ K_2O\\0.50\ CaO\\0.10\ BaO\\0.10\ ZnO\end{matrix}\right\}\ 0.35\ Al_2O_3\ \left\{\begin{matrix}3.20\ SiO_2\\0.15\ SnO_2\end{matrix}\right.$$

The glaze is better when the feldspar is calcined. The glaze is sprayed on; for good adherence, it should have a creamy consistency. The addition of ammonium salts thickens the glaze; a small addition of dextrin promotes smooth flowing. M.H.

Relative behavior of porous and dense fired porcelain insulators in high-frequency electric fields. WERNER ENDRES. *Keram. Rundschau*, **47** [41] 443–45; [43] 465–66; [45] 483–85; [47] 501–503; [49] 519–21; [50] 527–28 (1939).—Exhaustive experiments on the effect of the structure of porcelain insulators on their behavior at frequencies of 3×10^6, 2.82×10^7, and 7.83×10^7 cycles are described. It was found that porous porcelain contains, besides the usual bubbles filled with air or firing gases, fine cracks and fissures which lower the dielectric loss factor and dielectric constant. Completely dry porous porcelain heats less, therefore, than dense porcelain in the high-frequency fields. The reverse occurs if there is even the least trace of humidity absorption by the porous porcelain. Porous parts can therefore be located by measuring the temperature distribution on the surface of a specimen. The testing of insulators with high frequencies was found to be much superior to testing with 50 cycles, as the heating is much more pronounced in high-frequency fields. The test is more effective when it is made in a condenser field than when the insulator is made a condenser by metallic coatings. The time required for testing can also be reduced in this way. See "Results . . . ," *Ceram. Abs.*, **19** [8] 194 (1940). M.H.

Use of phosphate opacifying agents in sanitary-ware glazes. W. H. EARHART. *Bull. Amer. Ceram. Soc.*, **20** [9] 312–13 (1941).

PATENTS

Fuel injection spark plug. F. J. WIEGAND (Wright Aeronautical Corp.). U. S. 2,255,203, Sept. 9, 1941 (Feb. 28, 1940).

Service insulator. G. C. PRICE (Porcelain Products, Inc.). U. S. 2,254,978, Sept. 2, 1941 (Dec. 8, 1937).

Spark plug. C. E. MEYER (Soc. de Construction d'Appareils Mécaniques & Électriques pour Automobiles). U. S. 2,254,082, Aug. 26, 1941 (Feb. 24, 1940).

Spark plug and method of making. J. H. DILLON (Firestone Tire & Rubber Co.). U. S. 2,254,160, Aug. 26, 1941 (Dec. 29, 1939).

Equipment and Apparatus

A B C of drying. ANON. *Brick & Clay Record*, **95** [3] 30–31 (1939).—Periodic and progressive types of driers are discussed. Factors which affect the design and calculation of a waste heat drying system are presented. B.C.R.

Action of sprays. Coal Dust Research Committee of the Monmouthshire and South Wales Coal Owners Assn., Second Report. Abstracted in *Colliery Guardian*, **161**, 366–68, 389–92 (1940).—The most important factor, the water particle size, was measured by letting the mist fall into castor oil. Fifteen water sprays were tested, but only the results for the ten most efficient sprays are reported. These forced water through a small orifice, imparted a swirling motion, or both. A good spray produces particles averaging 250μ with a few as small as 40μ. These are not very effective on dust but are better for wetting roadways, etc. The addition of chemicals to reduce the surface tension gave little improvement. Nine compressed-air and water sprays were tested. The best had seven spray jets with water coming out the center of each and the air coming out concentrically around the water. An increase of the air to water ratio reduced the mist particle size at first, but further increase had no effect. This spray removed 80 to 85% of the dust in a dust cloud. The mist had an average particle size of 60μ but caught dust particles down to 2μ. The greater the relative velocity of the spray and dust, the higher is the efficiency of the mist. W.D.F.

Aerial ropeway and band conveyers at a brickworks. ANON. *Engineer*, **171** [4451] 293 (1941); reprinted in *Claycraft*, **14** [10] 247–50 (1941).—A disadvantage of ropeways is that the loading terminal, which is necessarily of heavy construction, cannot be readily moved about on the floor of the clay pit to follow up the receding clay face as excavation proceeds. A method is described which involves the use of belt conveyers for collecting the clay and delivering it automatically into the ropeway buckets. This is believed to be the first case of the use of a combination of multibucket excavator, conveyers, and an aerial wire ropeway. Illustrated. See "Interesting . . . ," *Ceram. Abs.*, **20** [10] 242 (1941). G.A.K.

Arc welding of crusher rolls. ANON. *Brick & Clay Record*, **96** [2] 27 (1940).—Worn crusher rolls may be repaired economically by welding metal onto the concave portion in the center of the rolls. B.C.R.

Colloid technique in ceramics. Modern vacuum deairing of clay in the extrusion press. OTTO MANFRED. *Ber. Deut. Keram. Ges.*, **19** [3] 103–105 (1938).—When M. previously spoke on the subject of colloid technique (*ibid.*, **15** [5] 256–68 (1934)), the question of the feasibility of vacuum deairing was raised. It is desirable for the material to pass through the vacuum space unhindered, but this can be only partially attained. As it is essential, in deairing, to expose many boundary surfaces to the action of the vacuum, there must be a great number of cutters. The flow of material will be retarded as little as possible if it passes through streamlined passages. W.H.H.

Economy in the design of exhaust systems. THEODORE HATCH. *Ind. Med. [Ind. Hyg. Sect.]*, **9** [10] 54–59 (1940).—The cost of controlling atmospheric contaminants released in manufacturing processes was carefully calculated for exhaust ventilation by H. It includes carrying charges on the initial investment, maintenance costs, cost of power and extra heat, and in some cases an extra labor charge resulting from interference with production by the control equipment. The most economical design of an exhaust system balances the carrying charges against the operating costs to give a minimum value. H. considers the various factors of design which together determine the power consumption and gives directions for reducing the power charge. These are summarized as follows: (1) reduce the magnitude of the forces of dispersion of the contaminant, thus decreasing the work to be done by the ventilating system; (2) provide exhaust hoods of the highest aerodynamic efficiency; (3) lay out the exhaust piping to give a balanced system; (4) employ the lowest possible safe transporting velocity in the pipes or, preferably, provide means other than pneumatic conveying for the removal of collected matter; (5) design hood entrances, elbows, junctions, enlargement sections, and other pipe details for minimum resistance; and (6) select air-cleaning equipment of sufficient capacity to insure an economical resistance. Power costs will thus be reduced 25% or more, insuring longer life to the system and lower maintenance costs. In some cases these savings will represent clear gain; in others they will more than offset the increased initial cost. The successful application of these principles, however, requires the use of more fundamental engineering concepts than those now applied to the design of exhaust systems. 12 references. K.R.

Jigger-tool life increased fourfold by heat-treating at 1850°F. ANON. *Ceram. Ind.*, **37** [1] 35, 38 (1941).—A hardening process developed by the Homer Laughlin China Co., Newell, W. Va., increases the life of jigger tools for automatic jigger machines. A new automatic brusher for removing grains of sand or small clay particles left from

the bisque firing handles 1000 dozen small pieces per hour and 600 dozen 7-in. plates per hour. Connected with the brushing machine is an automatic trademark stamper. A decalcomania washing machine handles 150 dozen plates hourly. Illustrated. H.T.

Lapp puts gravity to work in novel dust collector. ANON. *Ceram. Ind.*, **36** [6] 68, 70, 72 (1941).—A description of various machines and operations at the Lapp Insulator Co., Inc., plant at LeRoy, N. Y., is given. A unique dust-collecting system underneath the specially designed turning lathes saves power and reclaims scrap turnings. A homemade drier of high efficiency and a large jigger for forming chemical porcelain vessels are described. Illustrated. H.T.

Law of size distribution. STEWART S. FRITTS. *Rock Products*, **44** [5] 64–66, 90 (1941).—F. discusses the theory of grinding as a phase of the problems dealing with surface-area measurement of cement and cement raw materials. Equations and means of obtaining the necessary data for them to determine the actual mean diameter of the 0 to 7.5μ fraction are given; from these data the surface area may be determined. B.C.R.

Measuring surface area in grinding. FRED C. BOND. *Amer. Inst. Mining & Met. Engrs. Tech. Pub.*, No. 1296; *Mining Tech.*, **5** [2] 7 pp. (1941).—When a homogeneous comminution product is separated into fractions with a constant geometric ratio to each other and the log per cent weight retained is plotted against log diameter, a straight line results with a slope, m, the distribution modulus. This line can be extended to include small particles if it is assumed that no other small particles are present. The log per cent cumulative weight passing any screen plotted against log diameter gives a straight line parallel to the distribution line. The coarser sizes often make a hump which rises above the straight line. If there is a particle-size limit, the plotted line will curve under the straight line. The grind limit and the surface area can be calculated. An example of the evaluation of a screen analysis is given. This depends on the existence of a grind limit at a diameter near the colloid range and below 1μ. Particles below this size are assumed to have been present already divided but partially locked. This can be tested. It is found that the grind limit is 0.7μ with ores ground to different sizes and even with different ores. The energy necessary to grind quartz to this limit is about the same as that required to melt it. This plotting of two curves gives a more accurate value of the slope and also indicates any excess or deficiency of fines in the sample. W.D.F.

New units of crusher capacity and crusher efficiency. ARTHUR F. TAGGART. *Amer. Inst. Mining & Met. Engrs. Tech. Pub.*, No. 1297; *Mining Tech.*, **5** [2] 5 pp. (1941).—The capacity of a crusher depends on the crusher setting, size of feed, fines, moisture, and method of feeding. This is expressed by $T_R = TR_{80}KK'K''$. T_R, reduction tons per hour, is the new capacity unit. T is hourly weight of feed coarser than the coarsest discharge. R_{80} is 80% reduction ratio and is the aperture that would pass 80% of the feed divided by the aperture passing 80% of the product. K, K', and K'' are kind of rock, moisture, and method of feeding, respectively. R_{80} may be estimated from tables given if it cannot be measured. K is 1.0 for limestone, 0.85 for granite, and 0.75 for trap or diabase. K' is 1.0 but may fall to 0.5 or less if the fines are wet enough to cake. K'' averages 0.5 and rarely exceeds 0.75. The efficiency unit proposed is reduction tons per horsepower-hour and is $E_e = T_R/P$. P is horsepower consumed. E_e is fairly constant for one crusher. Examples are given for the calculation and use of E_e. W.D.F.

Oxyacetylene processes cut mine maintenance costs. H. C. STELLING. *Mining Congress Jour.*, **27** [7] 24–28 (1941).—Oxyacetylene is used chiefly for (1) hard-facing, (2) welding, (3) cutting, (4) gouging, and (5) flame-hardening. W.D.F.

Practical application of automatic heat and humidity controls to driers. R. R. ROBINSON. *Bull. Amer. Ceram. Soc.*, **20** [9] 309–11 (1941).—3 figures.

Proposed new type of pyrometer for measuring gas temperatures. A. BLACKIE. *Jour. Sci. Instruments*, **18** [6] 113–15 (1941).—The type of pyrometer consisting of a number of thermocouples of different thicknesses is examined with the purpose of establishing a system by which the true temperature of a flowing gas can be determined with a single reading. Having established the conditions, B. considers the practical difficulties of design and means for minimizing them. He discusses a resistance thermometer for measuring gas temperatures and describes the circuit diagram for such an instrument. 2 figures. J.L.G.

Sampling devices. NATHAN C. ROCKWOOD AND BROR NORDBERG. *Rock Products*, **43** [10] 39–40 (1940).—The construction of a Geary-Jennings sampler is described. Modifications of this device are suitable for sampling either slurries or dry materials. A device for sampling from a Fuller-Kingon transport line or from a screw conveyer is also described. B.C.R.

Scope and economics of electrostatic separation. H. LESLIE BULLOCK. *Ind. Eng. Chem.*, **33** [9] 1119–23 (1941).—Historical development, the theory of electrostatic separation, and the action of the fundamental separator are reviewed. Difference in the behavior of conductors and nonconductors, materials of different dielectric strength, and materials subject to pyroelectric charge are outlined. Attention is called to the possibilities of electrical and chemical conditioning of the feed and to the possible improvement of separation through the selection of proper supporting surfaces. Development work by the U. S. Bureau of Mines and individual investigators on the apparatus used and conditioning of the feed, improvements in plant air conditioning, and improved electrical apparatus will aid further development. A separator using non-conducting electrodes to promote safety, uniformity of field, and more precise regulation of field strength has recently been developed. The costs of four installations and a list of products being commercially separated by electrostatic separators are given. Illustrated. F.G.H.

Single strand wire saw. OLIVER BOWLES AND P. DE VITRY. *Amer. Inst. Mining & Met. Engrs. Tech. Pub.*, No. 1336; *Mining Tech.*, **5** [3] 5 pp. (1941).—A wire saw for cutting various stones has a single twisted ribbon strand. It carries more abrasive when new and retains this ability better than previous saws. It runs at almost twice the speed of previous saws and therefore cuts much faster. Silica sand is generally used, but garnet sand gives satisfactory results. W.D.F.

Standard screen scale. A. O. GATES. *Eng. Mining Jour.*, **142** [7] 51 (1941).—G. suggests the use of logarithmic cross-section paper with equally spaced lines having the values 1, 1.25, 1.6, 2.0, 2.5, 3.2, 4, 5, 6.3, 8, and 10 or multiples of these. More accurate plotting is possible with this arrangement. A standard sieve scale is suggested with the log of the numbers varying by 0.2000. This would give meshes per meter of 100, 160, 250, 400, 630, and 1000, corresponding to the openings, in millimeters, of 10, 6.3, 4, 2.5, 1.6, and 1. By letting 1 in. = 25 mm., the same series of numbers could be used to express the inch measurements. The value $^1/_{1.6}$ might be adopted for the ratio of hole opening in screen to distance between centers of wires. W.D.F.

Supersonic cell fluorometer. H. B. BRIGGS. *Jour. Optical Soc. Amer.*, **31**, 543–49 (1941).—The Debye-Sears diffraction effect has been adapted to the measurement of the rise and decay of luminescence in phosphors where times are of the order of a few millionths of a second. Results are given for calcium and cadmium tungstates, ZnS-CdS, and two long-lag phosphors. A.P.

Workers' bonuses easier to figure with speedometers on conveyers. ANON. *Ceram. Ind.*, **37** [1] 43–44 (1941).—The enameling department of the American Stove Co., St. Louis, Mo., uses conveyer speed ratings for the determination of the amount of ware processed. This method makes it easy to keep accurate records of the productivity of each worker and also permits quick determination of group bonuses without an actual count of the parts in the shop. Brief descriptions of various operations, such as pickling, firing, inspection, and de-enameling of defective ware by sandblasting, are given. Illustrated. H.T.

SEPARATE PUBLICATIONS

Mechanized Mining Brings New Electrical Hazards. E. J. Gleim and H. B. Brunot. *U. S. Bur. Mines Information Circ.*, No. 7160, 11 pp. Free.—The authors discuss the electrical hazards in mechanized conveyer mining caused by greater liberation of gas, more coal dust thrown into suspension, damage to trailing cables, use of more than one machine at a time in one space, sparking, overheating, or conductors. R.A.H.

Softening Water with Nonmetallic Minerals. S. J. Broderick. *U. S. Bur. Mines Repts. Investigations*, No. 3578, 18 pp. Free.—B. explains the importance of nonmetallic minerals in purifying and softening water and lists the minerals used. R.A.H.

Theoretical Calculations for Explosives: I, Explosion Temperatures and Gaseous Products and the Effects of Changes in Carbonaceous Material. F. W. Brown. *U. S. Bur. Mines Tech. Paper*, No. 632, 21 pp. Supt. of Documents, Washington, D. C. Price 5¢.—The approximate explosion temperatures and gaseous products are computed for a typical permissible high-ammonium nitrate explosive and a 60% gelatin dynamite. The effect of pressure on the explosion temperature and gaseous products is examined in detail, and the effects of changes in wrapper and carbonaceous material are considered. R.A.H.

PATENTS

Apparatus for blunging and decolorizing clay. S. C. Lyons (Bird Machine Co.). U. S. 2,255,429, Sept. 9, 1941 (July 28, 1937).—Apparatus of the class described consists essentially of an electrolytic cell provided with a plurality of pairs of relatively rotatable coaxial disks arranged in confronting horizontal planes and clearing each other by a small gap, at least one disk of a pair being a cathode, means for causing relative rotation between the disks, a permeable diaphragm defining and surrounding a cathode compartment in which the disks are located, an anode outside of the compartment, means for introducing liquid to be electrolyzed into the cathode compartment near its bottom, and means for withdrawing electrolyzed liquid from the anode compartment near its top, the disks defining a zigzag path of flow for the liquid introduced near the bottom of the cathode compartment to the top of the compartment, and the path of flow including in part the gaps between the disks.

Electric furnace. F. H. Norton (Babcock & Wilcox Co.). U. S. 2,255,518, Sept. 9, 1941 (Nov. 15, 1938).

Method and apparatus for forming clay products. H. S. Orth, C. R. Oberst, and W. E. Cramer (Industrial Ceramic Products, Inc.). U. S. 2,256,216, Sept. 16, 1941 (Nov. 3, 1938).

Mulling apparatus. E. O. Beardsley and W. E. Naylor (Beardsley & Piper Co.). Can. 398,572, Aug. 12, 1941 (July 23, 1938). G.M.H.

Packaging sagger pins. H. S. Orth, C. R. Oberst, and W. E. Cramer (Industrial Ceramic Products, Inc.). U. S. 2,256,215, Sept. 16, 1941 (Nov. 26, 1937).

Kilns, Furnaces, Fuels, and Combustion

Circular porcelain kilns with remote gas firing. F. Dietrich. *Keram. Rundschau*, **47** [15] 159–61; [17] 184–87 (1939).—The conversion of kilns from coal firing to gas firing, the gas being obtained from central gas plants some distance away, and the points to be considered in constructing new porcelain kilns are discussed. Several constructions are described, heat balances are developed, and operating results are given. The thermal efficiency amounted to 21 to 32.6%. See "Remote . . . ," *Ceram. Abs.*, **19** [4] 98 (1940). M.H.

Defective firing in pottery kilns and its causes. Albert Baier. *Keram. Rundschau*, **47** [4] 33–35 (1939).—The differences between firing with wood and coal are discussed in detail. M.H.

Function of water in the operation of firing. Karl Otto Schulz. *Ziegelwelt*, **71**, 265–66 (1940); abstracted in *Chem. Zentr.*, **1940, II**, 2524.—The water vapor present in fire aids in the production of salt glaze, among other things, by assisting in the decomposition of the NaCl. When the Na_2O steam formed comes in contact with the surface of the sintering body, the Na_2O combines with the alumina-containing silicic acid to form the salt glaze with the formation of soda alumina silicate. If the temperature does not reach 100°, mist or deposition of moisture occurs, which injures the charge. If the water contains sulfate, the mortar of the chimney may be destroyed by the formation of calcium sulfoaluminate (cement bacillus). M.V.C.

Latent energy and dissociation in flame gases. W. T. David, A. S. Leah, and B. Pugh. *Phil. Mag.*, **31**, 156–68 (1941).—The gases remaining after flame has spread through an inflammable gaseous mixture are not just hot gases but are believed to contain a considerable latent energy which, in the absence of surface, persists for a long time. Experiments with mixtures of carbon monoxide and air indicated that this latent energy probably resided in a proportion of the triatomic molecules formed during combustion as an excess of intramolecular energy which could not be handed to the translational degrees of freedom. Further experiments showed that there was a much larger dissociation in flame gases than in normal gases of the same composition under similar conditions of temperature and pressure. The extent of the abnormal dissociation varied with the latent energy. R.H.

Properties of free fusible material in coal ash as an index of clinker and slag formation. G. B. Gould and H. L. Brunjes. *Trans. Amer. Inst. Mining & Met. Engrs.*, **139**, 364–83 (1940); *Tech. Pub.*, No. 1175.—The softening temperature of coal ash has been used as an indication of the tendency of the coal to clinker, but it is not reliable, as the ash is mixed before the heat is applied. Six coals were crushed to 4-mesh and separated into four gravity fractions (less than 1.3, 1.3 to 1.4, 1.4 to 1.5, and over 1.5); each of these was separated into seven size groups (+4, 4 to 8, 8 to 16, 16 to 30, 30 to 50, 50 to 100, and −100). The ash content and ash-softening temperature were determined on each of the 28 samples. It was then possible to determine the fusibility of the ash from each class of material and also the distribution of the fusible material. Coals with similar conventional ash-softening temperatures differ greatly in the distribution and proportions of fusible materials. The six coals would be arranged in nearly the same order, regardless of the test used, but with some exceptions. These exceptions show why the regular test does not always work. The ash in many coals is sharply divided into ash fusible below 2200°F. and that fusible over 2700°F. Gravity separations made from 1.3 to 1.9 on coal ground through 200-mesh showed that the ash from coal sinking in 1.9 is very fusible as is also the small proportion floating in 1.3. The most important factor in predetermining the slagging of coal is the amount of free fusible material, generally that sinking in 1.9. W.D.F.

Protective gas atmospheres in electrically heated tunnel kilns of the fine ceramic industry. Erich Schirm. *Keram. Rundschau*, **47** [19] 205–207; [20] 218–20 (1939).—Protective atmospheres for ceramic products are generally of a reducing nature, as in the metal industry, and must be produced independently of the fuel in the case of electric heating, which is coming into wider use. By arranging oil or gases in the zones of a tunnel kiln where a particular effect is desired, the required atmosphere is created in the electric kiln by disintegration or combustion of the oils or gases. Several constructions are described. M.H.

Triple-track electric tunnel kiln installation. Rittgen. *Keram. Rundschau*, **47** [25] 275–78 (1939).—An 800-kw. kiln with three tracks is described in detail. The inner

track runs opposite to the two outer ones and operates at 1160°C. for glazed earthenware. The outer tracks operate at 1300° for biscuit ware and sanitary porcelain. The useful firing channel section is 700 x 800 mm., and the kiln is 90 m. long. The cold material is placed in the kiln and gradually heated to the highest temperature in the center of the kiln; it is then slowly cooled and leaves the furnace almost cold. The heating elements for the inner track are of Ni Cr (good for about 1100°C.), and those for the high-temperature outer zones are of silicon carbide (Globar or Silit). The voltage across the kiln is 380 volts (a.c.), and the temperature is automatically held constant to ±5°C. The operating cost per day amounts to Rm. 197.15, while that of gas-fired muffle kilns amounts to Rm. 101.18 and Rm. 185.57 per day and that of a circular coal-fired kiln is Rm. 323.24, including operation, repairs, and energy consumption for auxiliaries. The kiln was installed by the Societa Ceramica Italiana and has been operating for three years; the capacity is 12.5 to 15 tons of ware per 24 hr. with an energy consumption of 16,000 kw. M.H.

BOOKS AND SEPARATE PUBLICATIONS

Applied Heat Transmission. HERMAN J. STOEVER. McGraw-Hill Book Co., New York, 1941. 226 pp. Price $2.50. Reviewed in *News Ed.* (Amer. Chem. Soc.), **19** [16] 943 (1941). F.G.H.

Carbonizing Properties and Petrographic Composition of No. 1 Bed Coal from Bell No. 1 Mine, Sturgis, Crittenden County, Ky., and the Effect of Blending This Coal with Pocahontas No. 3 and No. 4 Bed Coal. J. D. DAVIS, D. A. REYNOLDS, R. E. BREWER, G. C. SPRUNK, AND L. D. SCHMIDT. *U. S. Bur. Mines Tech. Paper*, No. 628, 45 pp. Supt. of Documents, Washington, D. C. Price 10¢. R.A.H.

Constancy of B.t.u. Value of "Pure" Coal. J. F. BARKLEY AND L. R. BURDICK. *U. S. Bur. Mines Repts. Investigations*, No. 3572, 10 pp. Free. R.A.H.

PATENT

Electric arc furnace electrode control. WILLIAM HARVEY PAYNE. Can. 398,382 and 398,383, Aug. 5, 1941 (Feb. 3, 1941). G.M.H.

Geology

Bauxite and aluminum. ISTVÁN VITÁLIS. *Természettudományi Közlöny*, **72**, 129–35 (1940); abstracted in *Chem. Zentr.*, **1940, II**, 1629.—Types of Hungarian bauxites and suitable processes for extracting Al, Al_2O_3, and cement are described. M.V.C.

Bentonite in drilling. ANON. *Chem. Eng. & Mining Rev.*, **33** [394] 302 (1941).—In Australia, bentonite is used extensively in both rotary and percussion drilling. Bentonite introduced into water lines tends to stop leaks from cracks or poor joints. See *Ceram. Abs.*, **20** [1] 27 (1941). B.C.R.

Characterization of the mineral clay montmorillonite by the ultramicroscope. W. EITEL AND O. E. RADCZEWSKI. *Naturwissenschaften*, **28** [25] 397–99 (1940).—Na montmorillonite (natural bentonite from Wyoming) was prepared by sedimentation, and the fraction smaller than 0.5μ was studied in the electron microscope at 20,000 to 30,000 magnifications. Unlike kaolinite, no defined structure was visible, but a rather diffuse picture showed typical indications of a two-dimensional gel. After base exchange produced by shaking 18 hr. with the 0.01 *N* solutions of CsCl, $BaCl_2$, and $LaCl_3$, typical grains of individual crystals appeared. See "Ultramicroscopic . . . ," *Ceram. Abs.*, **18** [8] 222 (1939). J.M.N.

Corundum in South Africa. ANON. *S. African Mining & Eng. Jour.*, **51**, 567, 569 (Jan. 25, 1941).—Corundum is one of the few minerals, possibly the only one except gold, of which South Africa is the world's principal source of supply. In 1926 the production reached 6000 tons, but by 1938 this had dropped to 1500 tons annually. The mineral occurs in original or primary deposits (so-called "reef corundum") and in secondary deposits known as "eluvial corundum." A.G.S.

Flotation of barite from Magnet Cove, Arkansas. JAMES NORMAN AND BENJAMIN S. LINDSEY. *Amer. Inst. Mining & Met. Engrs. Tech. Pub.*, No. 1326; *Mining Tech.*, **5** [3] 5 pp. (1941).—The barite occurs mixed with quartz in shale; it contains submicroscopic carbonaceous material. Liberation of the barite from the quartz is not complete when 100% passes a 325-mesh sieve. A Raymond mill product, 98% passing 200-mesh, was ground in a steel-ball mill with sodium silicate added at the rate of 16 lb. per ton. The discharge went to a conditioner, where coconut fatty acid (3.33 lb. per ton) was added, and then to the flotation cells. Pine oil (0.33 lb. per ton) was added to the fourth cell. The concentrate was above 98% $BaSO_4$, and 90% of the $BaSO_4$ was recovered. Calcination at 1000°C. for 2 hr. destroyed the carbonaceous material. W.D.F.

Further investigations in the improvement of clays through control of pH and character of base-exchange saturation. GEORGE J. BARKER AND EMIL TRUOG. *Jour. Amer. Ceram. Soc.*, **24** [10] 317–22 (1941).—5 references, 3 figures.

Kaolin, Inc., producer of Carolina clay and mica. A. H. HUBBELL. *Eng. Mining Jour.*, **142** [7] 56–59 (1941).—Near Spruce Pine, N. C., is a kaolin deposit one mile square, the result of the kaolinization of an alaskite intrusive. Mining is done by open-pit methods; there is an average of 10 ft. of overburden. A scraper loads the clay onto a conveyer. The clay passes into a roll disintegrator while a deflocculating agent is being added to the water for treating the clay. The clay and water go into a blunger where long knives on a shaft agitate the mixture. Wheels with buckets scoop up coarse material and deliver it to a trommel with a 4-mesh screen. The +4-mesh gravel is sold; the −4-mesh has mica separated out, and some of it is sold. The clay overflow goes to single-deck screens with either 50- or 70-mesh screens. The oversize is mica and sand, and the mica is floated off. The clay is in the undersize plus some impurities. The clay then passes through a sand reel, which washes, dewaters, and conveys it; more mica and sand separate. The clay goes to a 7- x 30-ft. settling tank, $4\frac{1}{2}$ ft. deep, and settles 5 to 7 hr. The overflow passes through 200-mesh rotary screens to a launder where a flocculating agent is added and then to settling tanks where the water is decanted. The clay is filtered, and the cakes are dried at 170°F. for 22 hr., leaving 5% moisture. The mica recovered is dewatered, dried, and sized. W.D.F.

Measurement of particle size by the X-ray method. A. TAYLOR. *Phil. Mag.*, **31**, 339–47 (1941).—The difficulty involved in measuring the true diffraction broadening caused by the diffraction of X rays by small crystallites is discussed. A simple relationship is shown to exist between the Jones method of determining the line broadening and the definition of Warren. T. shows how a sudden onset of growth in a small fraction of the crystallites in the specimen led to extremely high values of the particle size. To interpret the result correctly as a real growth of the entire specimen or as merely an increase in the percentage of the portion greater than 1000 a.u. in size, the use of a large (19 cm. in diameter) Debye-Scherrer camera was found to be essential. An approximate relationship between the apparent fractional increase in particle size and the weight fraction of the specimen greater than 1000 a.u. was developed. R.H.

Operating characteristics of mechanical flotation machines. P. MALOZEMOFF AND R. H. RAMSEY. *Eng. Mining Jour.*, **142** [3] 45–49 (1941).—The study of several machines working on a copper ore resulted in new concepts about their operation. The prime purpose of the machine is to provide proper and adequate aeration of the pulp. Direct bubble-mineral contact is all that is needed, and flotation takes place wherever bubbles and mineral particles are in motion. Tests show that the capacity of flotation machines is directly proportional to the volume of the

pulp charged with air. This can be increased by lowering the impeller, but too much lowering allows the small bubbles to coalesce into large bubbles; these do not float the ore. Besides aeration, agitation has five effects on the pulp: (1) it prevents sedimentation; (2) it minutely subdivides the air; (3) it distributes the air uniformly; (4) it thoroughly mixes air, reagents, and pulp; and (5) it imparts sufficient velocity to particles and bubbles to produce the maximum chance of contact. Positive circulation of the entire pulp through the impeller is not necessary and may handicap the machine. An increase of froth area at the head of a bank of cells gave a better grade of concentrate; the scavenger cells, however, should have less froth area. In the flotation of nonmetallics, large froth areas are essential and a shallow tank design is indicated. W.D.F.

Optic properties of cordierite in relation to alkalis in the cordierite-beryl structure. ROBERT E. FOLINSBEE. *Amer. Mineralogist*, **26**, 485–500 (1941).—F. presents a chemical analysis of optically positive gem-quality cordierite from a newly discovered occurrence north of Great Slave Lake. Anomalies in the variation diagrams which relate the optic properties of cordierite to the iron-magnesium ratio are noted. The relation of the cordierite structure to that of beryl is clarified, and alkali-ion positions in the beryl structure are postulated. Alkalis have a pronounced effect on the optic properties of beryl, suggesting by analogy that anomalous variations in the optic properties of cordierite are due to variable alkali content. The suggestion is confirmed by graphical presentations of the optical properties of analyzed cordierites. W.D.F.

Practical aspects of particle-size control. S. C. LYONS. *Bull. Amer. Ceram. Soc.*, **20** [9] 303–306 (1941).—4 references, 4 figures.

Practice of evaluating kaolin. THEODOR EDER. *Keram. Rundschau*, **47** [1] 2–4 (1939).—Lixiviated or otherwise purified kaolins contain only traces of impurities which form the major part of the larger particles (200 to 30μ). An exact determination of the grain size, therefore, indicates the purity and, in the vicinity of the colloidal range, the fatness, plasticity, strength, and absorption. For grain sizes above 50μ, analysis is made by means of wet or dry sieves. A 10,000-mesh per cm.^{2} sieve (0.06-mm. openings) is suitable for evaluating kaolin, the commercial grades leaving residues of 0 to 10%. The determination of finer grain sizes is made by several methods, which are described briefly; they include the use of suspensions, sorting by wind (gravity), and the determination of viscosity. Two characteristic figures have been developed. The colloid number is defined as that percentage of kaolin or clay which is still in suspension at a height of 10 cm. in a special test glass after 2 hr. settling; a 5% kaolin suspension in distilled water is used for this test. The peptization number is defined as that percentage of kaolin or clay which is still in suspension at a height of 10 cm. after complete peptization. The exact procedure for making the determinations is given. M.H.

Prospecting, developing, and mining semiplastic fire clay in Missouri. R. S. BRADLEY AND B. K. MILLER. *Amer. Inst. Mining & Met. Engrs. Tech. Pub.*, No. 1328; *Mining Tech.*, **5** [4] 9 pp. (1941).—This clay occurs near Mexico, Mo.; it is of Pennsylvanian age. The top of the clay is fairly level, but its thickness varies from 5 to 40 ft. Deposits of clay are found by core drilling in favorable locations with holes on 800-ft. centers. If an area has suitable clay in several adjacent holes, it is drilled on 400-ft. centers and, if still promising, on 200-ft. and finally 100-ft. centers. Each core is sampled, and each sample is tested for (1) physical characteristics, (2) drying and firing shrinkage, (3) fired appearance, (4) fired bond, (5) reheat behavior at 2900°F., (6) pyrometric cone equivalent, and (7) chemical analysis. A cross section is drawn, showing the thickness and character of the clay. Stripping is done with a 1½-cu. yd. Diesel shovel loading 5-cu. yd. trucks. The average depth of stripping is 55 ft.; the cost is $0.145 per cu. yd. A tractor and a scraper are used for final cleaning of the top of the clay, and some bad clay is removed by hand. Clay faces 6 ft. high are mined by drilling and blasting. Three ¾-cu. yd. electric shovels load clay to three 3-cu. yd. dump trucks. The clay costs about 37¢ per ton delivered to the factory. The clay is sampled and tested at regular intervals. W.D.F.

Quartzite-like sandstone of the Banichskil deposits as raw material for the manufacture of silica brick. V. D. TSIGLER. *Ogneupory*, **9** [2] 94–100 (1941).—The characteristics of quartzite-like sandstones tested for their suitability in the manufacture of silica refractories are discussed. M.V.C.

Rarer constituents of South African fire clays. V. L. BOSAZZA. *Nature*, **147** [3737] 747 (1941).—B. found vanadium and molybdenum in South African fire clays but only traces or none at all of other rare oxides reported as clay constituents by other observers. Sulfur and phosphorus occur in these fire clays. See "Occurrence . . ." *Ceram. Abs.*, **20** [5] 126 (1941). J.L.G.

Stability of minerals in sedimentary rocks. P. G. H. BOSWELL. *Nature*, **147** [3737] 734–37 (1941).—B. discusses the origin of minerals in sedimentary rocks and the effect of sedimentary processes on their stability. J.L.G.

Structure of vitreous silica. S. S. LU AND Y. L. CHANG. *Nature*, **147** [3734] 642–43 (1941).—The authors took two series of photographs with copper Kα radiation. For one series they ground the silica to a powder and used a Debye-Scherrer camera. The other series was made on thin polished plates with the pinhole transmission method. The X-ray diffraction bands obtained in the two series differ in some respects. These differences are ascribed to the fact that glass regains a certain freedom of rearrangement during the powdering operation which causes certain changes in the structure. They verified this by taking a pinhole transmission photograph of a slab of powder which was found to be the same as the Debye-Scherrer photographs on powder samples. 3 photographs. J.L.G.

Textures of clays. V. L. BOSAZZA. *Nature*, **147** [3738] 779 (1941).—B. compares the particle-size analyses of two clays and shows that grain-size analysis without knowledge of the mineralogical composition of a clay is insufficient for predicting its plastic properties. The condition of the organic phases is also important in controlling the plasticity. J.L.G.

Use of low-percentage pyrolusite in the glass and enamel industries. LUDWIG STUCKERT. *Sprechsaal*, **73**, 265–67 (1940); abstracted in *Chem. Zentr.*, **1940, II**, 1630–31.—Oasin-Mangan with a low MnO_2 content can be used instead of high-percentage pyrolusite for smelting green, brown, and black glasses without appreciable alteration in the mix or working process. It is also possible to produce satisfactory black enamels, black art glazes, and a good black coloring substance for the ceramic and enamel industries. M.V.C.

Vermiculite and hydrobiotite. ROBERT F. RUTHRUFF. *Amer. Mineralogist*, **26**, 478–84 (1941).—A chemical analysis was made of hydrobiotite from Libby, Mont., and the indications are that it consists of alternate layers of vermiculite and biotite. Vermiculite and biotite give a silica-lamella residue when treated with hot dilute H_2SO_4. This silica was studied for its suitability as a catalyst substrate. Vermiculite (100 gm.) refluxed with 110 gm H_2SO_4 plus 220 gm. H_2O for 3 hr. gave 43 gm. of quite pure silica. Previous exfoliation of the vermiculite was of no value. Hydrobiotite treated similarly gave a similar residue plus some dark plates (biotite ?). Hydrobiotite exfoliates, on treatment with concentrated H_2SO_4 and exposure to air, because of the crystallization of the sulfate salts within the lamellas. W.D.F.

Xenolites of nepheline-syenites and alkali syenites in massive chibinite of the northern part of the Chibina Massives. N. A. VOLOTOVSKAYA. *Zapiski Vserossilskogo Mineralog. Obshchestva*, **68** [1] 45–68 (1939); abstracted in *Chem. Zentr.*, **1940, II**, 2139.—Among the xenolites studied the following groups are differentiated: coarse and medium grained nepheline-syenite, fine grained "agirit" nepheline-syenite, nepheline porphyrite, and alkali syenite. The origin of the minerals is discussed. M.V.C.

Zirconia in Brazil. W. MELZER AND G. H. CHAMBERS. *Foote-Prints*, **14** [1] 17–21, 24–26 (1941).—Near Cascata on the border between the states of Minas Geraes and São Paulo occur the world's only known commercial deposits of zirconium dioxide. Ores mined there include the "favas" type of waterworn pebbles; the compact "D-7" type, lower in iron and higher in silica; and an impure compact zircon. Mining, concentration, and transportation methods are primitive. The use of zirkite as a refractory is increasing as grades become standardized and the knowledge of physical and chemical properties grows. Ore reserves have been estimated at 1,790,000 tons. A.P.

SEPARATE PUBLICATIONS

Chromite. ROBERT H. RIDGWAY AND N. B. MELCHER. Preprint from U. S. Bur. Mines Minerals Yearbook, Review of 1940. Supt. of Documents, Washington, D. C. 12 pp. Price 5¢. R.A.H.

Clays. PAUL M. TYLER AND A. LINN. Preprint from U. S. Bur. Mines Minerals Yearbook, Review of 1940. Supt. of Documents, Washington, D. C. 16 pp. Price 5¢. R.A.H.

Exploration and Sampling of Domestic Deposits of Strategic Minerals by the Mining Division, Bureau of Mines. *U. S. Bur. Mines Repts. Investigations*, No. 3574, 7 pp. Free.—A report of progress as of May 1, 1941, on exploratory operations (begun Aug. 10, 1939, in seven different areas) on deposits of subcommercial or marginal grade strategic minerals is presented. See "Essential. . .," *Ceram. Abs.*, **19** [1] 28 (1940). R.A.H.

Feldspar. ROBERT W. METCALF. Preprint from U. S. Bur. Mines Minerals Yearbook, Review of 1940. Supt. of Documents, Govt. Printing Office, Washington, D. C. 10 pp. Price 5¢. R.A.H.

Magnesium. HERBERT A. FRANKE AND M. E. TROUGHT. Preprint from U. S. Bur. Mines Minerals Yearbook, Review of 1940. Supt. of Documents, Washington, D. C. 10 pp. Price 10¢. R.A.H.

Mineral Physics Studies. Ferromagnetic Properties of Hematite. Metallurgical Division Progress Report No. 47. EARL T. HAYES. *U. S. Bur. Mines Repts. Investigations*, No. 3570, 28 pp. Free.—H. presents the results of studies leading to the application of the knowledge of mineral physics to process metallurgy. He points out that hematite is ferromagnetic. R.A.H.

Minerals Yearbook, Review of 1940. U. S. BUREAU OF MINES. Supt. of Documents, Govt. Printing Office, Washington, D. C., 1941. 1459 pp. Price $2.00.—This edition contains the most comprehensive data ever assembled on the production, stocks, distribution, trade, and consumption of metals, nonmetals, fuels, and mineral products. R.A.H.

Ore-Testing Studies. Metallurgical Division Progress Report No. 45. A. L. ENGEL AND S. M. SHELTON. *U. S. Bur. Mines Repts. Investigations*, No. 3564, 28 pp. Free.—The results are presented of investigations on the composition, physical characteristics, and milling qualities of ores from various mining districts, including three from Nevada, two each from Arizona and Arkansas, and one each from Colorado, Idaho, Missouri, and North Carolina. **Metallurgical Division Progress Report No. 46.** EDMUND S. LEAVER, JESSE A. WOOLF, AND A. P. TOWNE. *Ibid.*, No. 3569, 84 pp. Free.—The results of tests on ores (primarily precious metals) are given for the purpose of furnishing information as to the most satisfactory method of treatment to obtain optimum economic recovery of the valuable minerals or metals. R.A.H.

Talc, Pyrophyllite, and Ground Soapstone. BERTRAND L. JOHNSON AND K. G. WARNER. Preprint from U. S. Bur. Mines Minerals Yearbook, Review of 1940. Supt. of Documents, Washington, D. C. 10 pp. Price 5¢. R.A.H.

PATENT

Treatment of clay. IRA WILLIAMS AND NATHAN MILLMAN (Sgoda Corp.). U. S. 2,255,371, Sept. 9, 1941 (April 16, 1940).—(5) The process comprises treating a clay slip, containing iron in solution and having a pH below 5 due to an acid stronger than carbonic acid, with calcium carbonate in an amount sufficient to increase the pH of the slip above 5 but insufficient to raise the pH of the slip to 7. (13) The process comprises treating a clay slip, containing iron in solution and having a pH below 4.5 due to an acid stronger than carbonic acid, with a strong water-soluble basic compound of an alkali metal in an amount sufficient to materially increase the pH of the slip but insufficient to raise the pH of the slip above 5 and then with a carbonate of an alkaline-earth metal in amount sufficient to increase the pH of the slip to at least 5.5 but insufficient to raise the pH of the slip to 7.

Chemistry and Physics

Chemistry and thermodynamics of aluminum and magnesium products. W. D. TREADWELL. *Schweiz. Arch. Angew. Wiss. Tech.*, **6** [3] 69–77 (1940).—In the Bayer process, $Al(OH)_3$ derived from an aluminate is precipitated by a condensation reaction. The polymerization process can be observed by electrometric titration and simultaneous observation of the viscosity and cloudiness of the sol. When precipitating clay with sodium carbonate and calcium carbonate to obtain Al_2O_3, a silicoaluminate of Na (sodium clay) is formed, followed by an orthosilicate of Ca and a calcium carbonate salt of Al which can easily be hydrolyzed and transformed into $CaCO_3$ and a water-soluble aluminate. Excess alkali is regenerated by hydrothermic decomposition. In the Haglund process, the solubility of Al_2O_3 in a very small quantity of aluminum sulfide is explained as a peptization, probably with the formation of a sulfoaluminate complex. The eutectic in the system Al_2O_3–Na_3AlF_6 is not a simple physical solution but probably a mixture of $1Na_3AlF_6 + 3Na(OAlF_2)$. T. determined the equation of the equilibrium $MgO + Cl_2 \rightleftarrows MgCl_2 + {}^1/_2O_2$ for pure $MgCl_2$ and for carnallite and calculated the sensitivity of the bath to air. The vapor pressures of $MgCl_2$ and KCl are newly determined. The tension of decomposition of the $MgCl_2$ bath and the carnallite is expressed as a function of the temperature, and values of free energy of formation are given for MgO and Al_2O_3. Using these results, T. considers the possibilities of producing the two by C reduction of the oxides. While additional electrolytic energy is needed for Al, it should be possible to produce Mg from the oxide with C reduction in high vacuum. An easily attainable yield of 70 to 75% should make this process superior to the $MgCl_2$ electrolysis. J.M.N.

Colorimetric determination of copper with ammonia—spectrophotometric study. J. P. MEHLIG. *Ind. Eng. Chem., Anal. Ed.*, **13** [8] 533–35 (1941).—A spectrophotometric study shows that the ammonia method for the colorimetric determination of copper is very satisfactory with few limitations. The procedure of Yoe is recommended. F.G.H.

Determination of pyrolusite and pyrolusite substitutes. E. O. PRIMBSCH. *Emailwaren-Ind.*, **18** [15–16] 36–37 (1941).—The moisture content is determined as follows: 1 gm. finely powdered substance is dried on a watch glass at 108° to 110° in a drier to constant weight (at least 2 hr.). To determine the silicic acid and manganese contents, 0.5 gm. of the sample is weighed in a 300-cc. beaker and dissolved by heating with about 40 cc. strong HCl. The residue should be almost white. When no more dark grains can be found in the insoluble part, several cubic centimeters of concentrated nitric acid are added, and the mixture is heated until the disappearance of the chlorine odor, usually after 10 min. (test with potassium iodide starch paper); it is thinned with double the quantity of water and filtered through a filter free from ash into a 250-cc. measuring flask. The filter is washed 2 or 3 times with

hot dilute HCl and then washed with hot water until the disappearance of the chlorine reaction. The filtrate is left to cool while the filter is ashed with the residue in a platinum crucible. The crucible is heated sharply to redness to constant weight, and, after weighing, the contents are evaporated with about 2 cc. hydrofluoric acid and 2 drops concentrated H_2SO_4; it is again quickly heated to redness. If there is much residue, as is usually the case with pyrolusite substitutes, the evaporation must be repeated; the silicic acid evaporates as SiF_4, and the loss in weight is the SiO_2 content. The 250-cc. measuring flask containing the cooled filtrate is filled to the mark with cold water and shaken well. Of the solution, 50 cc. (corresponding to about 0.1 gm.) is pipetted into a 500 cc. Erlenmeyer flask. The manganese content is determined in the solution diluted up to 300 cc. by the Volhard Wolff method which is as follows: The contents of the flask are heated to boiling, and a few cubic centimeters of 2% ferric chloride solution are added. Zinc oxide combined with water (1 part ZnO to 3 parts water) is added a little at a time, and the flask is constantly shaken; care must be taken to avoid too great an excess in the analysis. As soon as the precipitate begins to flake, enough ZnO has been added; a large excess will make the solution turbid, and the transition point in titration will be hard to recognize. A slight excess is harmless. The temperature is lowered by the addition of the ZnO, and, as the analysis yields exact results only when titrated at a temperature above 80°, the solution is boiled a short while. It is then titrated with a 0.1 *N* potassium permanganate solution which has been previously standardized against a manganese solution of known content. The permanganate solution flows in a thin stream into the flask, which is shaken constantly until the disappearance of the rose color is retarded. From this point on, the $KMnO_4$ solution is added 1 cc. at a time until the change occurs. When the approximate amount has been determined, 50 cc. are pipetted from the measuring flask, and the procedure is continued exactly as before. An amount of $KMnO_4$ 2 cc. less than that used before is added, and the solution is titrated with the addition of 5 drops until the end (1 cc. 0.1 *N* $KMnO_4$ solution = 1.648 mgm. Mn). If the value found for the manganese is converted into that for MnO_2, more than 100% is obtained. This proves that a part of the manganese must exist in low molecular compounds. There are several methods for the determination of the pure MnO_2 content. The usual method is the ferrosulfate method, but for the enamel industry, the simpler oxalate method is suitable: 0.5 gm. (1 gm. for pyrolusite substitutes) is heated in a 400-cc. Erlenmeyer flask with 50 cc. 0.5 *N* oxalic acid and about 20 cc. dilute sulfuric acid and dissolved. The insoluble residue must be free from dark particles. It is diluted with hot water to about 200 cc., and the excess oxalic acid is titrated back with 0.5 *N* $KMnO_4$ solution. One cc. of the amount of 0.5 *N* oxalic acid used corresponds to 21.732 mgm. MnO_2. When pyrolusite substitutes are analyzed, the titration is disturbed by a considerable amount of undissolved turbid constituents; it is therefore best to filter off these before titration. M.V.C.

Determining metallic iron in iron oxides and slags. JOHN P. RIOTT. *Ind. Eng. Chem., Anal. Ed.*, **13** [8] 546–49 (1941).—An investigation was undertaken to devise a new scheme which would eliminate the shortcomings of the mercuric chloride and copper sulfate methods of metallic iron analysis. Reliable results were obtained by using a feebly acetic acid solution of cupric potassium chloride in a carbon dioxide atmosphere. The fundamental feature of the method is the solution of iron by the cupric chloride of the reagent. F.G.H.

Fluxing properties of lithia. N. J. KREIDL. *Foote-Prints*, **14** [1] 1–11 (1941).—Sodium and potassium fluxes exert undesirable effects on chemical resistivity, electrical properties, and thermal expansion. Reasons why partial replacement of NaKO by Li_2O helps to overcome these faults are advanced on the basis of atomic structures, ionic potentials, and viscosity-temperature curves. Rough calculations demonstrate that only one-third the volume of lithia is required to confer the same fluxing power as compared with sodium. A glass base for vitrifiable colors with low melting point, high durability, and high gloss has the following formula:

$$\left.\begin{array}{l} 0.9\ PbO \\ 0.05\ K_2O \\ 0.05\ Li_2O \end{array}\right\} \quad 1.5\ SiO_2$$

An acid-resistant porcelain enamel has the following composition: $66.9SiO_2$, $3Al_2O_3$, 7.3CaO, 1.1ZnO, 18.7NaKO, and $3Li_2O$. A remarkable increase in resistivity and in viscosity takes place when 14% of the total alkali is replaced by lithia. In glasses, lithia additions should be balanced by increasing Al_2O_3 to maintain the expansion coefficient. The glass industry applies lithia to eliminate lead in special low-melting heat-resisting glasses, such as electric-lamp stems and tubing and opal glass. The use of lithia in decorating colors on glass has tended to weaken the bottle because of base exchange with sodium ions from the bottle. Suggested cures include adding kaolin or alumina to vitrifiable colors containing lithia. A.P.

Improvement in the "partition method" for the determination of boron. FRANCIS W. GLAZE AND ALFRED N. FINN. *Jour. Research Nat. Bur. Standards*, **27** [1] 33–37 (1941); RP 1401. Price 5¢.—In a previous method (*Ceram. Abs.*, **15** [8] 234 (1936)) it was found that barium, fluorine, iron, and zinc interfere. It has now been found that the substitution of sulfuric acid for hydrochloric acid eliminates the interference of all of these elements except fluorine and gives results no less satisfactory than the previous method. The new procedure should, therefore, be substituted for the older one when boron is to be determined in a glass of unknown composition or when the interfering elements are present. R.A.H.

Reactions in the solid state. P. GILARD. *Rev. Universelle Mines*, **16**, 159–64 (1940).—Reactions between solid bodies occur in ceramic and metallurgical processes and in geological phenomena. In the firing of clays, considerable structural modifications can be observed even at temperatures well below the fusion point. By reactions in the solid state a great many substances can be produced which cannot be obtained by liquid reactions. SiO_2 reacts with the alkali-earth oxides at temperatures as low as 400°C.; the reaction of lime with sillimanite at 550° gives metasilicates of Ca and Al. To produce such reactions, molecular interpenetration is necessary. This can be obtained either by very high pressures (up to 20,000 atm.) or by a liquid (which need not be water) or any crystalline substance. The various theories on this subject by Jander, Tammann, and others are outlined. Two conditions are indispensable for solid-state reactions: (1) the heat of formation of the product must be low, and (2) a sufficiently great difference must exist between the sum of the specific heats of the substances participating in the reaction and the specific heat of the reaction product. The reactions become more active with increasing temperature, and the manner of contact, velocity of diffusion, manner of propagation of the reaction, solubility of one substance in the other, and precipitation of new crystals play an important part. The ceramic industry makes frequent use of solid-substance reactions, e.g., between lime, silica, and alumina. By heating lime and silica to about 650°C., four silicates can be obtained, depending on the temperature and the mixture. The formation of cement is another reaction of solid substances. Under the effect of heat, $CaCO_3$ and $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ transform at a temperature well below the fusion point into CaO and CO_2 and Al_2O_3 and SiO_2. Beginning at 650°, numerous reactions take place: CaO and Al_2O_3 give $CaO \cdot Al_2O_3$; $2CaO \cdot SiO_2$ is formed; $CaO \cdot Al_2O_3$ binds a supplementary amount of CaO and forms $3CaO \cdot Al_2O_3$; $2CaO \cdot SiO_2$ takes on a molecule of CaO and gives $3CaO \cdot SiO_2$; and, finally, $3CaO \cdot 2SiO_2$, $5CaO \cdot 3Al_2O_3$, and $3CaO \cdot 5Al_2O_3$ are formed. As soon as the tricalcium compounds appear, fritting or fusion takes place, which accelerates the reaction. 17 references. M.H.

Routine determination of phosphorus and sulfur in coke—catalytic nitric-perchloric acid digestion method.

LOUIS SILVERMAN. *Ind. Eng. Chem., Anal. Ed.*, **13** [8] 524–25 (1941).—An improved procedure for the wet determination of sulfur in coke and an original procedure for the determination of phosphorus are given, the newer theories on the structure of coke being used as a basis for the method. The digestion acids are nitric and perchloric, not perchloric acid alone. F.G.H.

Scattering of light by pigment particles. D. H. CLEWELL. *Jour. Optical Soc. Amer.*, **31**, 521–27 (1941).—Variations in optical properties of a pigment caused by variations in particle sizes are corfelated with the scattering coefficient by an empirically derived equation which can be applied over a wide range of sizes and refractive indices. A.P.

Separation of calcium nitrate from strontium nitrate by monobutyl ether of ethylene glycol. H. H. BARBER. *Ind. Eng. Chem., Anal. Ed.*, **13** [8] 572–73 (1941).—In separating and identifying barium, calcium, and strontium after these elements have been precipitated as carbonates, use is made of the differential solubilities of the salts of the alkaline earths or the selective solubilities of organic reagents on the anhydrous chlorides or nitrates of these metals. While the different procedures have given fairly satisfactory separation of the three alkaline earths, they have not offered a clear-cut and positive separation. Although the differential solubilities of the alkaline-earth salts cannot be changed appreciably by varying the concentration of the separating reagents, the selective solubility of organic reagents on the anhydrous chlorides or nitrates should afford a positive separation if a reagent could be found which had a high solvent action on, e.g., the nitrate of calcium, and a negligible, or exceedingly low, solvent action on the nitrate of strontium. B. has found that calcium nitrate is completely and easily separated from strontium nitrate by the use of the monobutyl ether of ethylene glycol. The hydrated calcium and strontium nitrates and the reagent are rendered anhydrous by boiling the nitrates in the reagent (boiling point 170.6°C.). The solubility of anhydrous calcium nitrate in the reagent is 2.43×10^{-1} gm. per ml., while the solubility of the anhydrous barium and strontium nitrates in the anhydrous reagent is not more than that of strontium carbonate and barium sulfate in water. An analysis of 25 unknowns of the alkaline and alkaline-earth groups, using 1 drop of the unknown solution of 0.1 *M* concentration, gave results 100% correct and without uncertainty as to the presence or absence of the alkaline-earth metals. F.G.H.

Silicate analysis—criticism and suggestions. BÜTTNER. *Keram. Rundschau*, **47** [10] 101–102 (1939).—B. discusses the two most familiar analyses: (1) dissolving with $CaCO_3 + NH_4Cl$ according to the J. Lawrence Smith method, and (2) dissolving with $HF + H_2SO_4$ according to the method of Berzelius. A modification of the former, whereby $CaCO_3$ is replaced by $BaCO_3$, seems in many cases to be an improvement, giving more complete and quicker dissolving. In general, the first method and its modifications are preferable in case the silicate contains Mg, boric acid, or P_2O_5. It is, however, not very fast, and the results depend greatly on the manner of heating, for which no general instruction can be given. The Berzelius method does not have this disadvantage and requires less time; it can therefore be used with greater assurance of satisfactory results. M.H.

States of silicic acid. FRITZ BONTE. *Keram. Rundschau*, **48** [46] 381–84; [49] 416–17 (1940).—Seven modifications of crystallized silicic acid are known; they occur in nature principally as quartz. Normally, quartz occurs as the β modification with a specific gravity of 2.65. The β modification is transformed at 575° into the α modification. Another crystallized form is γ-tridymite (specific gravity 2.32 to 2.28) which at 117° is transformed into β-tridymite; this, in turn, is transformed into α-tridymite at 163°. Another crystallized form is β-cristobalite with a specific gravity of 2.32; this is transformed at 230° into α-cristobalite. Besides the crystallized forms of SiO_2, amorphous forms exist, e.g., quartz glass, which is obtained by melting any other modification; anhydrous silicic acid, which is obtained by dehydration of water-containing SiO_2; and opals and diatomaceous earth. A transition of crystallized and amorphous SiO_2 is flint, a modification of chalcedony. The diagram of the state of SiO_2 is established, representing the vapor pressure of the various modifications as a function of temperature, but this has a purely theoretical value as the vapor pressures are very small. The three principal temperature schemes can be expressed as follows:

$$\beta\text{-quartz} \overset{575^\circ}{\rightleftharpoons} \alpha\text{-quartz} \overset{870^\circ}{\rightleftharpoons} \alpha\text{-tridymite} \overset{1470^\circ}{\rightleftharpoons} \alpha\text{-cristobalite} \overset{1710^\circ}{\rightleftharpoons} \text{quartz glass},$$

$$\gamma\text{-tridymite} \overset{117^\circ}{\rightleftharpoons} \beta\text{-tridymite} \overset{163^\circ}{\rightleftharpoons} \alpha\text{-tridymite} \left[\overset{440^\circ}{\rightleftharpoons} \alpha_1\text{-tridymite}\right],$$

$$\text{and } \beta\text{-cristobalite} \overset{\text{about } 230^\circ}{\rightleftharpoons} \alpha\text{-cristobalite}$$

The transformations are influenced greatly by the transformation velocity. Slowly progressing irreversible transformations (quartz into tridymite or cristobalite) give a satisfactory silica product (brick) only if no further change of volume takes place in the mass; furthermore, satisfactory silica products can be obtained only if they are of such SiO_2 modification that the temperature changes to which they are exposed in service will not cause any suddenly occurring transformations. This can be represented as follows:

Transformation temp.	Transformation of . . . into	Change of vol. (%)	Change of length (%)
	(A) Suddenly occurring transformations		
	Reversible		
575	β-quartz $\rightleftharpoons$ α-quartz	2.4	0.8
117	γ-tridymite $\rightleftharpoons$ β-tridymite	0.6	0.2
230 (approx.)	β-cristobalite $\rightleftharpoons$ α-cristobalite	5.6	1.9
	(B) Slowly occurring transformations		
	Irreversible		
870	α-quartz$\rightarrow$$\alpha$-tridymite	12.7	4.2
1350	α-quartz$\rightarrow$$\alpha$-cristobalite	17.4	5.8
575, 870	β-quartz$\rightarrow$$\alpha$-tridymite	15.1	5.0
575, 1350	β-quartz$\rightarrow$$\alpha$-cristobalite	19.8	6.6
1470	α-tridymite$\rightarrow$$\alpha$-cristobalite	4.7	1.6
1710	α-cristobalite$\rightarrow$melt	0.1	0
575, 1350, 230	β-quartz$\rightarrow$$\beta$-cristobalite	14.2	4.7
1710	β-quartz$\rightarrow$melt	19.9	6.6
575, 870	β-quartz$\rightarrow$$\gamma$-tridymite	13.9	4.6
163, 117			

M.H.

System $2CaO \cdot SiO_2$–$K_2O \cdot CaO \cdot SiO_2$ and other phase-equilibrium studies involving potash. WILLIAM C. TAYLOR. *Jour. Research Nat. Bur. Standards*, **27** [3] 311–23 (1941); RP 1421. Price 10¢.—This investigation was undertaken to determine the manner in which K_2O is combined in Portland cement clinker. The present research on the phase-equilibrium relations of $2CaO \cdot SiO_2$ and $K_2O \cdot CaO \cdot SiO_2$ was made after preliminary examinations had shown that the compound $K_2O \cdot Al_2O_3$ was unstable in the presence of $3CaO \cdot SiO_2$ and $2CaO \cdot SiO_2$. The compounds $2CaO \cdot SiO_2$ and $K_2O \cdot CaO \cdot SiO_2$ were found to form a binary system containing one additional compound having the probable composition $K_2O \cdot 23CaO \cdot 12SiO_2$. Thermal, optical, and X-ray diffraction data are presented, and a temperature concentration diagram has been constructed. The stability of the compound $K_2O \cdot 23CaO \cdot 12SiO_2$ in Portland cement clinker prepared only from K_2O, CaO, Al_2O_3, and SiO_2 has been indicated. While no evidence of any other compound of potash in such preparations, heated and cooled under equilibrium conditions, has been

obtained, it has been indicated that SO_3 present in a mixture combines with K_2O to form K_2SO_4. This compound has since been observed in many commercial clinkers. R.A.H.

Thiocyanate method for iron—spectrophotometric study. J. T. Woods with M. G. Mellon. *Ind. Eng. Chem., Anal. Ed.*, **13** [8] 551–54 (1941).—By means of a spectrophotometer a critical study has been made of the colored system resulting from the interaction of ferric and thiocyanate ions. From several hundred spectral transmission curves obtained, of which those shown are representative, the following conclusions relating to the use of this procedure for the colorimetric determination of iron are evident. Ammonium thiocyanate is preferable to thiocyanic acid as a color-forming reagent. Nitric acid is preferable to sulfuric or hydrochloric acid. With this acid, Beer's law is followed through the pH range 1.2 to 1.5 but not in higher acidities. Many of the 57 diverse ions studied interfere. The sensitivity is increased approximately 100% by using a 60% acetone solution. This compound also improves the stability of the color. A solution of two cobaltammine salts is an improved color standard except for a slight fading after several months. In general, the thiocyanate method is inferior to several others, especially those using *o*-phenanthroline, α,α'-bipyridyl, or mercaptoacetic acid. Illustrated. F.G.H.

BOOKS

Index to the Literature on Spectrochemical Analysis. American Society for Testing Materials, Philadelphia, Pa., 1941. 2d ed. 96 pp. Price $1.00. Reviewed in *News Ed.* (Amer. Chem. Soc.), **19** [14] 805 (1941). F.G.H.

Polarography. I. M. Kolthoff and J. J. Lingane. Interscience Publishers, Inc., New York, 1941. 510 pp. Price $6.00. Reviewed in *News Ed.* (Amer. Chem. Soc.), **19** [16] 942 (1941).—Polarographic methods of analysis are described in detail. F.G.H.

PATENT

Titanium pigment production. J. E. Booge (E. I. du Pont de Nemours & Co.). U. S. 2,253,551, Aug. 26, 1941 (June 22, 1938).

General

Appraisal of vision in industry. H. S. Kuhn. *Ind. Med.*, **9** [9] 456–58 (1940).—The eyes of industrial workers are now being studied in personnel and training departments to estimate their efficiency and for safety and compensation records needed by the company. The first industry to focus attention on vision was aviation; 50% of the applicants proved unable to meet the eye requirements. Eye tests call for a technique based on a binocular test rigidly controlled and standardized to avoid unfairness or inaccuracy; tests must be available which will furnish the data needed for any job, together with a special technique for interpreting eye requirements for special jobs that may be reinterpreted on transfer to other jobs. In the Calumet area an industrial survey of 16,000 individual workers showed that 1724 employees had uncorrected acuity defects. These acuity defects ranged from 14.8% in some plants to 38% in others. Of the employees, 15% showed a fairly uniform average defect in depth perception; about 6% showed a color deficiency. Muscle imbalance, which averaged 25%, is explained and illustrated. With management and industries beginning to appreciate the importance of visual correlation in plant efficiency, industrial medicine departments are urged to keep ahead in progressive practical service and the setting of standards. K.R.

Ceramic industry in Nationalistic Spain. A. Müller-Bergh. *Keram. Rundschau*, **47** [2] 17 (1939).—Most of the ceramic factories are established near the Bay of Biscay and in the Asturian Alps. Some fine ceramics are made in the south near Seville, where large earthenware factories also exist. The economic situation is discussed at length. It is now practically impossible to obtain raw materials which were formerly imported, owing to lack of foreign trade. The demand for ceramic ware is greater than the capacity of the plants. M.H.

Chest fluorography with portable X-ray equipment on 35-mm. film. W. Palmer Dearing and Alexander E. Turner. *U. S. Pub. Health Repts.*, **55**, 2369–77 (Dec. 27, 1940).—The cost of routine Roentgen examination of the chest is almost prohibitive when unselected adult groups require such examination, although it discloses appreciable numbers of previously unsuspected cases of treatable pulmonary tuberculosis. Tuberculin tests, though much cheaper, are always refused by a portion of the population, while another portion will not return for further readings. The one procedure which accomplishes the objectives of X-ray chest examination at a far lower cost is fluoroscopy (suggested by Caldwell in 1911), which consists of photographing the X-ray shadow on a fluoroscopic screen. The authors undertook the development of a 35-mm. film technique for survey work in rural areas with portable equipment loaned by the Westinghouse X-ray Co. They describe and illustrate the camera unit in action, discuss comparative techniques and details, showing results at varying focal distances, and reproduce six chest photographs. More than 1500 persons have been examined, with both conventional films and microfilms. In cooperation with the Tennessee State Department of Public Health, 121 cases and family contacts were recorded by both regular X-ray and 35-mm. films in six county health department clinics; 88 of these have been tabulated. The Metropolitan Life Insurance Co., in certain pre-employment examinations, has estimated that fluoroscopic screening lacks about 13% of the accuracy of the full-sized radiograph, but they continue its use as a practical and economical procedure in bringing the advantages of chest examination to communities and individuals who would otherwise be passed by. K.R.

Correct illumination means increased efficiency. P. W. Peel. *Glass*, **18** [6] 168, 171 (1941).—P. discusses the importance of adequate illumination in industry, cleanliness as an aid to better lighting, and the elimination of glare. Both local and general lighting systems are included in the discussion. B.C.R.

Diagnosis of lead poisoning. R. A. Kehoe. *Baltimore Health News*, pp. 154–55 (1941). F.S.M.

Effect of vitamin C on workers exposed to lead dust. S. W. Marchmont-Robinson. *Jour. Lab. Clin. Med.*, **26**, 1478–81 (June, 1941).—A group of 303 employees engaged in the assembly of automobiles and exposed to inhalable lead dust varying from 3 to 15 mgm. per 10 cu. m. of air was given 50 mgm. of ascorbic acid (vitamin C) daily in chewing gum. After a short period there was a noticeable decrease in muscular fatigue and an improvement in spirits and efficiency. The authors suggest the possibility that the effect of lead on the human economy may be only indirectly toxic, the absorption of lead producing an avitaminosis C. This is the condition of vague symptoms known as chronic lead poisoning but is in reality chronic subclinical scurvy. F.S.M.

Wilhelm Eitel 50 years old. R. Rieke. *Ber. Deut. Keram. Ges.*, **22** [5] 201–202 (1941).—Dr. Eitel, Director of the Kaiser Wilhelm Institute for Silicate Research in Berlin-Dahlem, celebrated his 50th birthday on May 6, 1941. Since the founding of this institute (1926), so important to the silicate industry, Dr. Eitel has conducted it in a manner worthy of imitation, and under his guidance fundamental papers have been issued on glass, cement, ceramics, and silicate research in general. Dr. Eitel won special recognition for the comprehensive work "Physical Chemistry of the Silicates" (*Ceram. Abs.*, **20** [7] 183 (1941)). W.H.H.

William Lloyd Evans. William McPherson. *News Ed.* (Amer. Chem. Soc.), **18** [24] 1118–19 (1940); reprinted in *Bull. Amer. Ceram. Soc.*, **20** [9] 315–16 (1941).

Fluorine excretion in the urine in chronic fluorine intoxication of cryolite workers. G. C. BRUN, H. BUCHWALD, AND K. ROHOLM. *Acta Med. Scand.*, **106**, 261–73 (1941).—Fluorosis in workers grinding cryolite, first described in 1932, manifests itself as a generalized osteosclerosis. Absorption of the dust from the lungs is practically excluded, but in the acid medium of the stomach a third of the fluorine is liberated as fluorine ion. The absorbed fluorine ion is not taken up by soft tissues but only by the bones and teeth. As far as is known, its excretion is only through the urine. In the urine of 30 hospital patients on a normal diet, 0.8 mgm. fluorine was found per day (0.18 to 1.85 mgm.) or 0.92 mgm. fluorine per liter of urine. For 24 cryolite workers, however, the average fluorine excretion was 16 mgm. per liter (2.41 to 13.41 mgm.). Generalized osteosclerosis can be produced by the prolonged intake of 25 mgm. of fluorine per day. Even many years after a worker had left his job, his urine contained abnormally large quantities of fluorine, which shows that he mobilizes fluorine from its deposits in the skeleton. F.S.M.

Physical examinations of industrial workers. PAUL A. BREHM. *Wisconsin Med. Jour.*, Sept., 1940; reprinted in *Ind. Med.*, **9** [10] 535–38 (1940).—B. reviews the Wisconsin examination program of the Workmen's Compensation Dept. of the Wisconsin Industrial Commission. He explains and comments favorably upon the important medical features of the examinations which include (1) occupational and medical history, (2) vision and hearing, (3) foci of infection, (4) heart, chest, and abdomen, (5) enlarged glands and elevated temperature, and (7) laboratory tests. The duties of an examining physician are stressed; he must possess a knowledge of industrial plant processes and the conditions under which individual workers have been employed. K.R.

Recovery of carbon monoxide-poisoned monkeys under X-ray treatment. J. A. CAMERON. *Radiology*, **36**, 486–87 (April, 1941).—As X rays and strong light have been found to aid recovery from carbon monoxide poisoning in smaller animals, the authors experimented with stronger X rays on monkeys. In each test two monkeys were kept in an atmosphere containing carbon monoxide for the same time and were then removed and kept under the same conditions except that one was exposed to the X rays with its head protected. In 9 experiments with 12.5% carbon monoxide, two test animals died before the X ray could be applied, but the remaining 7 recovered on treatment with X rays; all those not so treated died. In other experiments, the same animal was exposed to sublethal carbon monoxide concentrations twice with an interval of a week or more between the two exposures, one of which was followed by X-ray treatment. In each case the recovery time was reduced by one-half by the treatment. F.S.M.

Renaissance of industrial hygiene. C. D. SELBY. *Amer. Jour. Pub. Health*, **30** [12] 1422–26 (1940).—Among the changes now occurring in industrial hygiene, the important features are as follows: (1) recognition of the fact that workmen are the primary beneficiaries and that the maintenance of their health must be the principal objective; (2) a knowledge that the benefits to industry are sufficiently cogent to justify the active interest of the management; (3) development of a wholesome rivalry among the professions concerned; (4) assumption of a public health viewpoint by those serving in health departments of industry and adoption by them of the methods of preventive medicine; (5) an awakening in the medical profession to the opportunities in ethically managed industrial health programs and an elevation of industrial health to a higher level of respect as a specialty in the science and practice of medicine; and (6) recognition of the necessity of employing industrial-hygiene procedures in developing an effective national defense. B.C.R.

Salt in drinking water. R. T. FORD. *Occupational Hazards*, **3**, 17–18 (April, 1941).—The Youngstown Sheet & Tube Co. has supplied salt with drinking water since 1935 for the prevention of heat sickness. An automatic device adds the required quantity of salt to each 2.5 gal. of water passing through the meter, and salt tablets are also dispensed to supplement the salt in the water and to be used at individually cooled fountains. The number of disabling heat cases in 1926 was 77; since salt dispensing was inaugurated, not a single case has occurred. F.S.M.

Silicosis claims. ANON. *Ohio Industrial Commission Monitor*, **14**, 308 (July, 1941).—Since silicosis was added to the list of compensable occupational diseases in Ohio, 724 claims for compensation have been filed with the Industrial Commission up to June 30, 1941. Of this number, 235 were allowed, 337 were disallowed, and 152 are still pending. Of the total claims allowed, 122 (51.9%) originated in foundries, 30 in steel foundries, 64 in iron foundries, and 28 in nonferrous foundries. Eighty-eight (37.5%) were filed by ceramic workers. Of these, workers in tableware filed 30, floor and wall tile 22, glasshouse refractories 9, electric insulators 6, insulating brick and silica brick 4 each, enamel, stoneware, and silica sand and diatomaceous earth 3 each, building brick and tile, firebrick, glass, and sanitary ware 1 each. Eighteen claims were filed by cut stone workers (7.6% of the total). Monument workers filed 13, building stone 4, and quarries 1. Four claims arose from polishing, buffing, and grinding, and 1 from coal mines; 2 were miscellaneous. F.S.M.

Treatment of lead poisoning with sodium citrate. S. S. KETY AND T. V. LETONOFF. *Proc. Soc. Exptl. Biol. & Med.*, **46**, 476–77 (March, 1941).—Sodium citrate removes lead ion from solution by the formation of a soluble complex of extremely low dissociation; for this reason, it is an eliminant of lead in poison cases. Charts and details of treatment are presented, showing that in six cases in which sodium citrate was administered, with and without other materials, there was a rapid disappearance of toxic symptoms and a fall of the lead content of the blood to normal. F.S.M.

BOOKS AND SEPARATE PUBLICATIONS

Analytical Chemistry of Industrial Poisons, Hazards, and Solvents. M. B. JACOBS. Interscience Publishers, Inc., New York. 661 pp. Price $7.00—This book brings together a great deal of useful information. Choices of several methods are offered in many cases to allow for individual preference and suitability. The references cited at the end of each chapter also augment the choice of procedures. The book is well printed on good paper and has both author and subject indexes. F.S.M.

Occupational Hazards and Diagnostic Signs. L. I. DUBLIN AND R. J. VANE. *U. S. Dept. Labor, Div. Labor Standards, Bull.*, No. 41, 70 pp. (1941). Supt. of Documents, Govt. Printing Office, Washington, D. C. Price 10¢. F.S.M.

Protecting Plant Manpower. ALICE HAMILTON ET AL. *U. S. Dept. Labor, Div. Labor Standards, Special Bull.*, No. 3, 70 pp. (1941). F.S.M.

Safe Practice in the Manufacture of Glass Sand. C. W. STEINBACH. *Penna. Dept. Labor & Ind., Safe Practice Bull.*, No. 75, 9 pp. (May, 1941).—The production of glass sand is described in detail, together with the dust-prevention practices used in each step of the process. F.S.M.

PATENTS

Composition of matter. F. A. MCCANN (Pacific Clay Products Co.). U. S. 2,254,301, Sept. 2, 1941 (May 17, (1940).—A composition of matter comprising particles of nonfibrous actinolite and a binder.

Production of polished surfaces. NOEL SHAW (Carbide & Carbon Chemicals Corp.). U. S. 2,253,587, Aug. 26, 1941 (Dec. 7, 1938).

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